

# REACTIONS



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F. A. FLÜCKIGER.

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DETROIT, MICH.



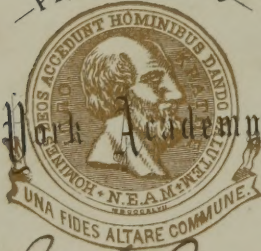
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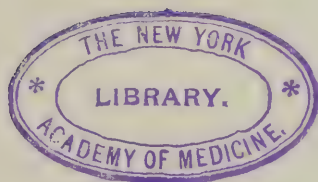
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Bonn, May 10th 1893

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Allow me to thank you for your very kind  
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No doubt your analytical work should  
be made available to the professor.

Now being about to dispatch my last  
contributions to your work, let me state that

I fully acknowledge how zealously and  
"intelligently" you not only translated,  
but in many many respects improved  
the "Reactions"

Believe me to remain

sincerely yours friend

F. A. Flückiger,

Professor Emeritus of the  
University of Strasbourg

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# REACTIONS.

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A SELECTION OF

**Organic Chemical Preparations Important to  
Pharmacy in Regard to their Behavior  
to Commonly Used Reagents.**

BY

**F. A. FLÜCKIGER,**

PH. D., M. D.

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TRANSLATED, REVISED AND ENLARGED

BY

**J. B. NAGELVOORT,**

Analytical Chemist to the Pharm. Chem. Laboratory of  
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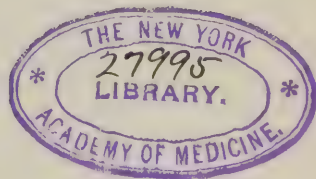
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## PREFACE OF THE AUTHOR.

The desire to be of some service to my colleagues, stimulated a publication of the following results. They were purposely obtained by simple methods. Together they form a series of unpretentious experiments, the meaning and full value of which could not have been explained consistently, unless by going into very elaborate details; and in these pages practical information only is aimed at. Most of the facts here described are, for this reason, given without theoretical explanation; moreover, such attempt would disproportionately enlarge the scope of this volume if given satisfactory elucidation. Some reactions, now described for the first time, are not yet fully understood; while others are explained by many of the text books of pharmaceutical or theoretical chemistry. Valuable information on this score is to be found in Dr. E. Nickel's book, "*Die Farbenreactionen der Kohlenstoffverbindungen*" (Zweite, Auflage, Berlin, 1890. H. Peters).

Many of the observations described have, however, been published before by me, as *e. g.* the reaction on morphin with bismuth subnitrate; but in many cases I relied partly on my predecessors. It is a recognized duty to give all authors credit for their work, but to do this in every instance would involve the quotation of the very voluminous literature perused without adequate benefit to the purpose intended. Most of these literary references are to be found in Beilstein's classic text book of Organic Chemistry ("*Handbuch der Organ. Chemie*," von Dr. F. Beilstein 3te Auflage 1893, Hamburg and Leipzig. Leopold Voss), or in Beckurts' Year Book of Pharmacy ("*Jahresbericht der Pharmacie*," Von Prof. Dr. H. Beckurts, Göttingen. Vandenhoeck & Ruprecht).\*

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\*For Americans, a compensation for those references is to be found in the "*Reports on the Progress of Pharmacy*," embodied in the proceedings of the *American Pharmaceutical Association*. Those reports, written with exceptional accuracy and admirable judgment, have just been published, for 1892, and are to be obtained, with the Proceedings, yearly, from the permanent Secretary of the A. P. A., PROF. JOHN M. MAISCH, 143 North Tenth Street, Philadelphia, U. S. A.—J. B. N.

The experiments described, as a rule, were made in broad daylight, usually at temperatures ranging from 14° to 20° C., and unavoidable differences in temperature or in light may be the cause of some variations in the results; it is impossible to make all the conditions alike, however desirable this might be; even the shape or kind of glassware or apparatus selected for the reactions may make a difference. But as quantity and volume, when of importance, are prescribed in detail, special selections of apparatus will easily be adapted accordingly. Small test tubes with a foot, about 7 cm long, 1 cm in diameter, and of a capacity of 6 c. c., are often the most useful. Sometimes the same are to be preferred of two (2) cm in diameter, in which one can filter a liquid without a funnel. It must be borne in mind also that there is a question only of C. P. articles. The identity reactions described in the following pages, are not to be relied upon where impurities of any kind are likewise to be considered, as is the case in toxicological analyses; and in the examination of galenical preparations. Every compound must be isolated *pure*, where positive identity is to be proved or a quantitative estimate required: but for the exact performance of tasks of this nature, a thorough knowledge of the behavior of chemicals, as laid down in the following pages, is an indispensable duty to the analyst.

My endeavors at accuracy in this respect will, I trust, therefore, prove to be useful to the profession, and promote the preparation and examination of many of the most important chemicals.

F. A. FLÜCKIGER,

*Now at Bern, Switzerland.*

Nov. 1891, Pharmaceutical Institute of the University at Strassburg.

## TRANSLATOR'S PREFACE.

---

This volume is a revised and enlarged edition of the German text—not a verbatim translation. Prof. Flückiger kindly favored me with a few additional notes from his pen. It is assumed that there is no necessity for describing apparatus, and that the English reader, no less than the German student, is familiar with chemical manipulations. Very elaborate and full information on many articles treated of in this small volume, in a modest way, appear in the recently published 2nd part of Vol. iii of Allen's *Comm. Org. Analysis* and in Guareschi's "*Introduzione allo studio degli alcaloidi*," Torino 1892.\* Where the statements of Allen and Flückiger or other authorities are not concordant, I have given the results of personal experience. This has given me an opportunity to decide some few moot problems in analytical work.

The spelling adopted for scientific and chemical words is that laid down by the rules of the Am. Assoc. for the Advancement of Science, 1891. It will also be understood that the temperatures are given in centigrades.

It is suggested that all reagents be kept from the light. Even the  $\text{MnO}_4^-$  solutions preserve readily for a year in a dark place; and where such is convenient, they should be kept in amber-colored glass. It is well to bear in mind that pure ether or chloroform cannot be retained in good condition for analytical work in half-filled bottles on the shelves; also that much distilled water made in the laboratories, in automatic stills, contains traces of  $\text{NH}_3$  and is unfit for delicate reactions. Reactions on alkaloids are often best obtained on the lid of a small porcelain crucible.

Proceeding from the basis of Flückiger's teaching, the reader will receive what incidental service I am able to render as a con-

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\*See excerpts in the *Apotheker Zeitung*, of Berlin, by F. A. Flückiger, Nos. 103, 105, December 24th and 31st, 1892, and No. 1, January 4th, 1893. A German translation of Guareschi's excellent book will be issued early in 1894, by R. Gaertner (H. Heyfelder, Berlin.)



tribution to the intellectual thesaurus laid down in the "Reactions" without special mention. Where it is a necessity, where the reader has a right to expect it, writer's initials will be found in brackets.

The publisher has left abundant room for marginal notes, as a means of contributing to the value and usefulness of our work.

J. B. NAGELVOORT.

Detroit, U. S. A., 1893.

Pharmaceutic-Chemical: Laboratory of PARKE, DAVIS & Co.

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LIST  
OF  
PRINCIPAL REAGENTS USED IN THIS BOOK.

*Temperature 15° C.*

- 1 Ammonia water.**—Sp. gr. 0.96 = 10%  $\text{NH}_3$ .
- 2 Bromin water.**—Dissolve 1 g. of Br. in 30 c. c. of water.
- 3 Chlorin water.**—Should have a green tinge and be kept in a glass-stoppered bottle, standing up side down, in a dark place; it will keep, if thus preserved, for a long period.
- 4 Ferric chlorid solution.**—This solution must be free from uncombined HCl. Sp. gr. 1.281: Dissolve 29 g. of  $\text{Fe}^2 \text{Cl}^6$  in 71 c. c. of water
- 5 Hydrochloric Acid.** C. P.—1.124 sp. gr. = 25 HCl in 100.
- 6 Iodin water.**—A saturated watery solution of about 1 g. of I in 4 liters of water.
- 7 Iodin (0.5g) and potassium iodid (1.5g)** in 250 c. c. of water.
- 8 Kalium bromate.** ( $\text{KBrO}_3$ )—**Potassium bromate.**
- 9 Kallum iodate.** ( $\text{KIO}_3$ )—**Potassium iodate.**
- 10 Lime water.**—A saturated solution of calcium hydrate; contains about 1 g. CaO to the liter.
- 11 Mercuric cyanid.**—Dissolve 5 g. of  $\text{Hg}(\text{CN})_2$  in 30 c. c. of water.
- 12 Mercuric potassium iodid solution.**  $\text{HgI}_2 (\text{KI})_2$ .—Dissolve 22.70 g.  $\text{HgI}_2$  and 16.60 g. K I in one liter of water; keep a certain quantity of a solution of  $\frac{1}{10}$  of this strength.
- 13 Mercuric chlorid solution, 5%.** Dissolve 1 g.  $\text{HgCl}_2$  in 19 c. c. of water.
- 14 Mercuric bromid solution; about 0.5%.**—Dissolve 1 g.  $\text{HgBr}_2$  in 215 c. c. of water.
- 15 Nitric Acid** C. P. Sp. gr. of 1.185 = 30  $\text{NO}_3 \text{H}$  in 100.
- 16 Picric Acid; saturated solution.**—Dissolve 10 g. pure crystals of Trinitrophenol ( $\text{C}_6 \text{H}_2 (\text{NO}_2)_3 \text{OH}$ ) in 90 c. c. of water.
- 17 Potassium dichromate solution, 5%.**—Dissolve 2.5 g. of pure  $\text{Cr}_2 \text{O}_7 \text{K}_2$  in 47.5 c. c. of water.



- 18 Potassium ferricyanid solution, 5%.**—To be made fresh when wanted, by dissolving 1 g.  $K^3Fe(CN)^6$  in 19 c. c. of water.
- 19 Potassium ferrocyanid solution, 5%.**—Dissolve 2.50 g.  $K^4Fe(CN)^6 + 3H^2O$  in 47.5 c. c. of water.
- 20 Sodium hydrate solution** of 1.17 sp. gr. = 15% NaOH.—Do not make any larger quantity than 250 c. c.: Dissolve 35 g. of NaOH, from sodium, in 250 c. c. of water, and lubricate the glass stopper with vaselin.
- 21 Sulfuric Acid purissimum.** Sp. gr. 1.840; contains about 97%  $H^2SO^4$ .—Must not become colored with brucin, codein, morphin or papaverin; it is very difficult to obtain an acid of such purity, which fact must be taken into consideration, when a color-reaction appears with the acid.—Compare the articles named under each one's separate heading.
- 22 Sulfuric Acid containing chromic acid.**—Dissolve 0.02 g. of  $Cr^2O^7K^2$  in 10 c. c. of water and add to the solution 30 g. of conc.  $H^2SO^4$ : To be made fresh when wanted.
- 23 Sulfuric Acid containing potassium permanganate.**—Dissolve 0.02 g.  $MnO^4K$  in 10 c. c. of water and add 30 g. of concentrated  $H^2SO^4$  to the solution: To be made fresh when wanted.
- 24 Tannin solution.**—To be made fresh when required, by dissolving 1 g. of tannin in 19 c. c. of water.

## Acetanilid—Phenylacetamid.



### ANTIFEBRIN.

Odorless and colorless, unctuous laminæ of slight burning taste. Melting point  $113^{\circ}$ . Boiling point  $295^{\circ}$ . Soluble in 200 parts water at  $15^{\circ}$ , in 18 parts at  $100^{\circ}$ ; easily soluble in ether, alcohol, chloroform and benzene; very little in carbon disulfid.

(a) By boiling 0.50 g. of Acetanilid with five (5) c. c. of water, taking the test tube out of the flame and warming the turbid fluid after two minutes again, it clears up and the undissolved Acetanilid goes in drops to the bottom. The solution does not act upon litmus paper nor gives a reaction with ferric chlorid (Reagent 4).

(b) 0.10 g. Acetanilid heated with one (1) c. c. of sodium hydrate solution (Reagent 20) and three (3) drops of chloroform, gives off the offensive, poisonous, Phenylisocyanid,  $\text{C}^6\text{H}^5 \cdot \text{NC}$ ; (the isonitril reaction); the mixture becomes yellowish red by adding bromin water (Reagent 2).

(c) 0.10 g. Acetanilid is soluble in one (1) c. c. of sulfuric acid (Reagent 21). The solution remains colorless and clear, after the addition of three (3) c. c. water; but in an hour crystals of Acetanilid begin to form; sooner, when 0.20 g. Acetanilid has been taken for the experiment.

(d) If 0.10 g. Acetanilid is heated to boiling with one (1) c. c. of hydrochloric acid (Reagent 5), an equal volume of a saturated watery solution of phenol (compare *Phenol*, page 95), and also one (1) c. c. of a saturated watery solution of chlorinated lime is added  $\text{Ca} (\text{OCl})^2$ , a turbid red or violet fluid is obtained, turning dark blue on adding ammonia water (Reagent 91) in excess; (indophenol reaction).

(e) Treated with sodium nitrate ( $\text{Na NO}^3$ ) or nitrite ( $\text{Na NO}^2$ ), as described under "(c)" for *Phenacetin*, page 91, Acetanilid gives a bright red colored solution.

(f) One (1) c.c. of Reagent 22, shaken with 0.10 g. of Acetanilid, changes to an intense red color, immediately turning blue and soon fading.

(g) 0.10 g. of Acetanilid heated with two (2) c. c. sulfuric acid (Reagent 21) until light brown, cooled off, and mixed a little at a time with bromin water, (Reagent 2) gives a very light red colored fluid. Very soon an abundance of white, microscopically small crystal needles appear.

(h) 0.20 g. Acetanilid is not changed by two (2) c. c. nitric acid (Reagent 15); by warming it is dissolved, whereby a yellowish-red colored fluid is obtained; heating further to the boiling point does not change the color; when the test tube is kept for hours in the water bath, however, the hue changes to a dark brown red.

### **Aconitin.**

$C^{33}H^{45}NO^{12}$ .

Aconitin crystallizes in rhombic or hexagonal tables. Melting point  $183^{\circ}$  (Wright);  $186^{\circ}.5$  (Dunstan). Writer [J. B. N.] found pure, white, crystalline Aconitin, Trommsdorff, dry, to melt at  $186^{\circ}$ , and crystalline, yellow, Aconitin, Merck, dried previously, to melt at  $178^{\circ}$ .

Soluble in alcohol, ether, chloroform and benzene; sparingly soluble in cold, more freely in hot water; insoluble in carbon disulfid and ligroin. It has basic properties, not acting, however, upon litmus and phenolphthalein.

A (cold) watery solution of Aconitin has an alkaline reaction towards tincture coccionellæ (1:10).

(a) Dissolve 0.010 g. of Aconitin or of one of its salts, in one (1) c. c. nitric acid (Reagent 15); evaporate to dryness; add to the residue, when cool, a few drops of an alcoholic solution of caustic potash (1:5) and note the odor of benzoic ethyl-ester.

(b) Dissolve 0.10 g. of Aconitin, in two hundred and fifty (250) c. c. water, by aid of alcohol and a drop of acid. The utmost care in this manipulation is to be recommended. Transfer one (1) c. c. of this solution ("A") into a one hundred (100) c. c. flask. Dilute with water to one hundred (100) c. c. Four (4) c. c. of this

twice diluted solution ("B") held in the anterior part of the mouth for one (1) minute, then rejected and the mouth rinsed, gives usually, in from five (5) to fifteen (15) minutes a characteristic tingling sensation to the tongue, or on the lips with some.\* (1:250,000.)

The sensation of Aconitin, the physiological test on the epithelium of tongue or lips, suggests a feeling of having been burned; the solution is too strong when a tingling is felt. When no sensation is obtained, repeat the experiment with a less dilute solution ("B"), taking five (5) c. c. of solution "A" to make "B". Aconitin has been found to vary in physiological strength as 1:15; 37, 5; :100.† All these preparations give the same special and general alkaloidal reactions. The writer [J. B. N.] often found it necessary to dilute 1:400,000 for the above described physiological tests; commercial Aconitin was to me often distinctly bitter in a 1:250,000 dilution.

(c) To five (5) c. c. of above described solution "A", add a few drops of a five (5) per cent.  $\text{Au Cl}^3$  solution, when a voluminous precipitate is obtained. Collect, wash and dry it. Melting point  $135^\circ.5$ .

(d) To five (5) c. c. of solution "A" add twenty (20) c. c. of water and a few drops of Reagent 12. This gives no precipitate; an opalescence only.

(e) A few drops of a solution of iodine (4) in potassium iodide (8) and water (500 c. c.) gives in dilution "(d)" a voluminous precipitate.

Two less important reactions must be mentioned:

(f) 0.005 g. Aconitin gives a pink, sometimes a yellowish-red color reaction, with 0.010 g. Sugar and two (2) drops Sulfuric acid. Only *amorphous* Aconitin; crystallized A. does not give it. Compare Morphin, page 76, and Veratrin, page 152.

(g) An identity reaction on Aconitin, in fl. extr. of Aconit-root of good quality, is to be made as follows: Exhaust five (5) c. c. fl. extr.—when made alkaline—with ether. Evaporate ether; add 0.5 ( $\frac{1}{2}$ ) c. c. water to the residue of evaporation; warm; filter; add a few drops of the filtrate to two (2) c. c. of

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\* This test, known as Squibb's, was first observed by Dr. Headland (Wormley's *Microchem. of Poisons*, pages 628, II, 1885). It is an indefinite method of verifying the *strength* of Aconitin. A better one is given since by Allen in *Ph. J. and Transact.*, 1891, p. 230.

† Mededeelingen uit de Apotheek van het Ziekenhuis te Groningen door M. J. Schröder, in *Ned. Tydschr. v. Ph. Ch. & Tox.* Mei 1891, page 152, on Aconitin. Friedländer, Trommsdorff, Merck, Gehe and others.



Reagent 23. Rotate. A purple hue appears, disappearing in a few seconds; the color is restored on adding an additional five (5) drops of the reagent: fading again.

### **Amygdalin.**



Small laminæ or prisms, according to the process of crystallization. Warmed in a test tube, it gives off water and melts to a brown liquid, which solidifies to a clear, cracked mass; when the latter is heated it chars and produces brown colored vapors of an aromatic odor, suggestive of caramel.

(a) Those vapors give an acid reaction to moist litmus paper. Water shaken with charred Amygdalin, has also an acid reaction.

(b) Amygdalin is soluble in about twelve (12) parts water at normal temperature; and in one hundred and fifty (150) parts alcohol of 0.83 sp. gr., under the same condition; it is easily soluble in boiling alcohol and in hot water; nearly insoluble in ether, chloroform and carbon disulfid.

(c) A watery saturated ( $15^{\circ}$ ) solution of Amygdalin is neutral and not affected by the common reagents for alkaloids, it being a glucosid. One (1) part dissolved in two hundred (200) parts water is slightly bitter, one (1) c. c. of the solution being swallowed.

(d) 0.005 g. Amygdalin dissolved in five (5) c. c. of sulfuric acid (Reagent 21) gives a violet-red colored clear fluid; this color is permanent in the cold for a week; turns brown after that time. Warmed, it chars, and an odor of bitter almond oil is developed. Evaporated with hydrochloric acid (Reagent 5) Amygdalin gives a dark brown residue; with nitric acid (Reagent 15) it leaves a colorless residue.

(e) Amygdalin is soluble for hours without decomposition, in an alkaline cupric tartrate solution (Fehling's solution), in the cold; warming the same in a waterbath throws down cuprous oxid, whereby also ammonia,  $\text{NH}^3$  is developed.

Prepare the alkaline cupric tartrate as follows:

*Solution A*—Crystals of pure copper sulfate are powdered and pressed between filter paper; 34.64 g. are weighed and dissolved in

water; 0.5 ( $\frac{1}{2}$ ) c. c. of sulfuric acid (Reagent 21) added and the mixture diluted to 500 c. c. ( $\frac{1}{2}$  liter).

*Solution B*—One hundred and seventy-five (175) g. of Rochelle salt (potass. sodium tartrate) are dissolved in three hundred and fifty (350) c. c. water; filter; add to the filtrate a clear solution of fifty (50) g. caustic soda, from sodium, in one hundred (100) c. c. water. Dilute the mixture to 500 c. c. ( $\frac{1}{2}$  liter).

Preserve the solutions A and B separately and mix one (1) c. c. of each, for a reaction when wanted.

(f) 0.10 g. Amygdalin, warmed on a waterbath with 0.50 g. peroxid of manganese, two (2) c. c. sulfuric acid, and one (1) c. c. water, develops the pungent odor of formic acid; the fumes have an acid reaction to moist litmus paper. The mixture has an aromatic odor while cooling.

(g) 0.050 g. Amygdalin is dissolved in twenty-five (25) c. c. almond milk.—Two (2) sweet almonds with about thirty (30) c. c. water, suffices to make the emulsion for this reaction. Very soon the odor of bitter almond oil and of hydrocyanic acid is noticed. Prepare filter paper moistened with a dilute solution (1:2000) of copper sulfate and afterwards dried, then moistened again with a fresh alcoholic tincture of guaiacum wood, to prove that hydrocyanic acid is present; this paper, recently made, detects hydrocyanic acid, by becoming blue, in an atmosphere containing very small quantities of it.

(h) Take a few lumps of granulated zinc, such as is used in a Marsh or Gutzeit's apparatus; pour a proper quantity warm twenty (20) per cent. sulfuric acid over it and, when hydrogen develops quietly, dissolve 0.10 g. Amygdalin in the fluid. Very soon a strong aromatic odor will be noticed, due, as under (g) to benzaldehyd, disappearing when the previously decanted fluid is warmed with a drop of nitric acid.

**Andromedotoxin.****ASEBOTOXIN.**

Crystallizes in colorless needles. Melting point  $229^{\circ}$ , whereby it decomposes. Soluble in water (2.8 per cent at  $12.5^{\circ}$ ); in alcohol (0.821 sp. gr.) eleven (11) per cent.; in commercial amyl alcohol 1.14 per cent.; very little in chloroform; much less in ether; nearly insoluble in benzene and ligroin. Its watery solution has no reaction towards litmus. The usual reagents on alkaloids do not give a precipitate in it. It is a glucosid.

To verify identity reactions, take one hundred (100) c. c. fluid extract *kalmiæ latifoliæ*; expel alcohol; add lead subacetate solution in excess; filter; remove lead with  $\text{Na}^3\text{PO}^4 + 12 \text{ aq}$ ; filter; evaporate to a small quantity; exhaust with chloroform; evaporate chloroform. Purify by dissolving in dilute alcohol and adding an excess of ether, and separating the crystals; dissolve in water. Parts of this watery solution evaporate to dryness.

- (a) Warm with dilute  $\text{H}^2\text{SO}^4$ — dark red color;
- (b) Warm with dilute  $\text{H Cl}$ — yellow, green, violet colors;
- (c) Warm with dilute  $\text{H}^3\text{PO}^4$ — red brown color;
- (d) Warm with dilute  $\text{HNO}^3$ ; evaporate to dryness; expose to vapors of  $\text{NH}^3$ — turmeric yellow color.

**Anilin.**

Melting point— $8^{\circ}$ ; below— $8^{\circ}$  it is crystalline. Sp. gr. 1.036 ( $0^{\circ}$ ); 1.026 at  $15^{\circ}$ . Boiling point  $183^{\circ}$  (760 mm barometer). At normal temperature is a colorless oily fluid, of peculiar odor. Miscible in all proportions with ether, alcohol or chloroform; not in all proportions with carbon disulfid, or liquid paraffin; soluble in water 3.1:100 at  $16^{\circ}$ . (Böckmann.)

(a) A trace Anilin, stirred with a glass rod the size of a match, into two (2) c. c. of Reagent 22, colors the latter permanently blue. A watery solution of Anilin gives the same reaction, in course of time in the cold, quicker by warming. Neither chloroform, water, or carbon-disulfid dissolves the blue color.

(b) Agitate strongly two (2) c. c. Anilin with (50) c. c. water; filter. This solution has a sharp, aromatic taste, and is neutral to red litmus paper, alkaline to violet dahlia paper, coloring the latter green. It gives—by virtue of its faint alkalinity—a precipitate in five (5) per cent. solutions of ferric and ferrous salts, in five (5) per cent. zinc—and in five (5) per cent. alum salts.

(c) Potassium dichromate added in excess to Anilin solutions, acidulated with  $\text{H}^2\text{SO}^4$ , causes a dark green precipitate, turning black by further addition of the Reagent.

(d) Equal volumes of Reagent 11 and the watery Anilin solution yields a clear mixture, in which crystals soon form.

(e) A proper quantity of a watery Anilin solution added to about five (5) c. c. of Reagent 13, gives a crystalline precipitate of the combination  $(\text{C}^6\text{H}^7\text{N})^2\text{HgCl}^2$ .

(f) Three (3) c. c. of Reagent 12 and three (3) c. c. of the watery solution obtained under “(b)” cause no precipitate at first; very soon, however, crystalline needles form in the fluid; an amorphous precipitate is produced immediately if an excess of the Anilin solution is used, which precipitate is soluble by adding still more of the Reagent.

(g) The yellow fluid obtained by adding 0.001 g.  $\text{KClO}^3$  to five (5) drops sulfuric acid (Reagent 21) becomes blue violet when a few drops of a watery solution of Anilin is added; the color fades slowly to red, by diluting the mixture with water; ammonia (Reagent 1) restores the blue color.

(h) Chlorin water (Reagent 3) added to watery Anilin solutions gives violet colored fluids: bromin water white, blue red or dirty green colored ones.

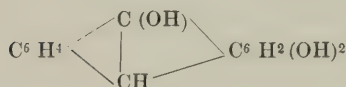
(i) Moisten a glass rod with sodium hydrate solution (Reagent 20) and hold this for a few minutes in the vapor of Cl in the chlorin water bottle; a trace of sodium hypochlorid is thereby formed. A watery Anilin solution stirred with this rod becomes of a dirty violet color; if the glass rod moistened with sodium

hydrate solution has been exposed to bromin vapors instead, the colors will be red-yellow; white, when iodin water is taken.

(j) A glass rod, moistened with hydrochloric acid (Reagent 5) gives off white clouds when held in a test tube containing a drop of Anilin. Stirring the Anilin with it, it forms a crystalline mass of Anilin hydrochlorid; when this is spread out on a mirror and a trace  $\text{K ClO}^3$  added, red, blue and green colors are obtained.

(k) Anilin gives the isonitril reaction described under “(b)”, article *Acetanilid*, by taking Anilin instead of acetanilid.

### Anthrarobin.



A brownish gray, amorphous powder. Heated in a glass tube, it gives off yellow brown vapors of acid reaction to moist litmus paper, also chars. It is soluble in ether and in alcohol with a yellowish brown color; less soluble in chloroform; insoluble in carbon disulfid.

(a) Water dissolves very little, even at the boiling point; the sharp pungent taste of the solid Anthrarobin can hardly be noticed in the yellow colored solution, which has an acid reaction to litmus paper; gives a dirty, green brown color with ferric chlorid (Reagent 4); reddish brown with lime water.

(b) Some of the watery solution, dropped on sulfuric acid (Reagent 21) gives a violet red color; on Reagent 22, it gives a more brown red color.

(c) Nitric acid (Reagent 15) decomposes Anthrarobin, whereby a brown red fluid and a dark brown solid mass is formed. Strewn upon Sulfuric acid, it colors this brown red.

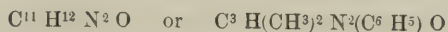
(d) Lead acetate and lead subacetate solutions give in the watery solution brown precipitates.

(e) Reagent 17 added to the watery solution gives a strong dark brown turbidity.

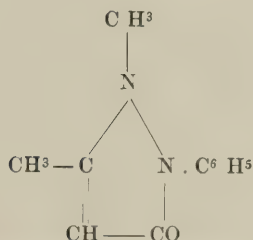


(f) 0.005 g. Anthrarobin, two (2) c. c. water, and five (5) drops ammonia (Reagent 1), give a greenish-brown color, changing to blue and violet.

**Antipyrin—Phenyldimethylpyrazolone.**



or



PHENAZONE: ANALGESIN.

Melting point 113°. Can not be distilled. Crystals of the monosymmetric system.\* Ten (10) parts Antipyrin are soluble in twelve (12) of water at 15°, and in half that amount at 100°; in thirteen (13) parts alcohol of 0.814 sp. gr. (15°); in equal parts of amyl alcohol; in one and a half parts chloroform; in fifty (50) parts ether; insoluble in petroleum spirit and in carbon disulfid. Its watery solution is bitter; limit 2:100; has no reaction to litmus paper; shows a trace of alkalinity when methyl orange is used as indicator,—that is to say: a ten (10) per cent. watery solution bleaches somewhat the pink color derived from the addition of a mineral acid to the fluid; ten (10) c. c. of Antipyrin solution have hardly an appreciable effect on fifty (50) c. c. of the pink colored water.

(a) Tannin (Reagent 24) causes a strong precipitate in a one (1) per cent. solution of Antipyrin.

(b) To ten (10) c. c. of a watery solution of Antipyrin one-half ( $\frac{1}{2}$ )

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\* Compare Roscoe and Schorlemmer, Vol. I, page 735.

per cent. add one (1) c. c. of picric acid solution (Reagent 16). No precipitation takes place in this dilution, but yellow prismatic crystals commence to form very soon. Picric acid causes an immediate precipitate in stronger solutions.

(c) To ten (10) c. c. of a two (2) per cent. watery solution of Antipyrin add five (5) c. c. Reagent 12; this gives a turbidity. No precipitation takes place in a five (5) per cent. solution, though in course of half a day feathery crystals are formed.

(d) One (1) c. c. of a five (5) per cent. mercuric chlorid solution (Reagent 13) added to four (4) c. c. of a two (2) per cent. Antipyrin solution, gives an amorphous precipitate, disappearing on warming slightly, reappearing when the fluid cools off. Mercuric bromid solution (Reagent 14) acts in the same way. Mercuric cyanid solution (Reagent 11) added to a saturated watery solution of Antipyrin gives no precipitate or turbidity. Neither does a potassium dichromate solution (Reagent 17).

(e) Sulfuric acid takes up considerable quantities of Antipyrin; even by warming; the acid remains colorless. But a small crystal of sodium nitrate ( $\text{Na NO}_3$ ) added to the mixture, produces a permanent yellow or reddish yellow color.

(f) Antipyrin, triturated with sugar, turns yellow when a few drops sulfuric acid are added to the mixture in the mortar.

(g) Two (2) c. c. of nitric acid (Reagent 15) dissolve, at  $15^\circ$ , 0.20 g. Antipyrin, without coloring; the slightest heat colors the fluid yellow, turning into a permanent red; this red solution, when spread out in a thin film, may be evaporated to dryness, without losing its color.

(h) A solution of 0.30 g. Antipyrin and 0.10 g. sodium nitrite ( $\text{Na NO}_2$ ) in 2.5 c. c. of water, turns greenish blue on the addition of ten (10) drops of acetic acid (1.064 sp. gr.); in course of an hour green crystals of nitrosoantipyrin,  $\text{C}_6\text{H}_5\text{N} < \begin{smallmatrix} \text{CO} \cdot \text{C} \cdot \text{NO} \\ \text{N} \cdot (\text{C} \cdot \text{H}^3) \text{C} \cdot \text{CH}_3 \end{smallmatrix}$ , appear in the fluid; the crystals are even bluish green by lamplight, and can be washed with cold water; they are largely soluble in slightly warmed acetic acid. The fluid is discolored by zinc dust.

(i) The same reaction occurs when Antipyrin is added to sweet spirit of nitre (ethyl nitrite) containing free acid.

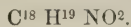
(j) 0.10 g. Antipyrin, 0.10 g. sodium nitrite ( $\text{Na NO}_2$ ) and 0.20

g. mercuric chlorid ( $\text{Hg Cl}_2$ ), shaken together with four (4) c. c. water, turn green (nitrosoantipyrin) in the course of an hour.

(k) Add one (1) drop of a saturated watery solution of Antipyrin, to one (1) c. c. of Reagent 4; this produces a flocculent precipitate soluble in water or alcohol to a blood red fluid. This color is still very distinct when diluted to two hundred (200) c. c.; sodium chlorid ( $\text{Na Cl}$ ) is conducive to the formation of the flocculent precipitate. A red, or yellowish red amorphous precipitate is formed on mixing one hundred (100) c. c. of a saturated watery solution of  $\text{Na Cl}$  with one (1) c. c. of a saturated watery solution of Antipyrin, and one (1) c. c. of Reagent 4 is added thereto.

(l) To five (5) c. c. of a ten (10) per cent. watery solution of Antipyrin, add chlorin water (Reagent 3); this causes a turbidity, immediately disappearing and especially noticeable along the sides of the test tube; in other words, it is soluble in excess of the Reagent; reappears after a while.

### **Apocodein.**



Is an amorphous, brown powder, that gives an alkaline reaction to moist red litmus paper. Soluble in ether, alcohol and chloroform; not soluble in carbon disulfid. By boiling a part with water, cooling off and filtering, a somewhat turbid filtrate ("A") is obtained, wherein Reagents 6, 12, 13, 16 and 24, give precipitates. It does not change in an alcoholic solution.

(a) Ferric chlorid (Reagent 4) gives a greenish-brown precipitate in an alcoholic solution of Apocodein, that is soluble in alcohol and in water.

(b) Reagent 4, added to Apocodein solution "A," gives a brown fluid, turning green.

(c) Chlorin water (Reagent 3) dissolves it with a yellow color, turning red after adding ammonia; (Reagent 1.)

(d) The following color reactions are given with acids: red-

brown with sulfuric (Reagent 21): red with nitric (Reagent 15): dark brown with sulfuric containing chromic acid (Reagent 22).

(e) Acetic acid added to a mixture of Apocodein with peroxid of manganese and water, turns the latter green; filter; agitate with chloroform; the color of the filtrate changes to blue, and a brown colored top layer is formed. Substituting peroxid of lead for the peroxid of manganese, one obtains a red-brown filtrate, which chloroform does not change.

(f) Apocodein gives somewhat similar color reactions to morphin with a mixture of 0.020 g. of ammonium molybdate and five (5) drops of sulfuric acid (compare "(d)" page 75); the color is, however, more brownish-black at first and changes slowly to blue. It is well to keep in mind the fact the Reagent itself turns blue after a certain time.

(g) Apocodein gives immediately blue precipitates with the Reagents described under "(g)" article *Morphin*.

(h) Apocodein gives a mirror with  $\frac{N}{10}$  silver solution; the test to be made in the dark.

(i) Dissolve 0.10 g. potassium iodate ( $KIO^3$ ) in five (5) c. c. water, add 0.005 g. Apocodein and finally five (5) drops acid acetic (1.06 sp. gr.); this produces a yellowish fluid, changing to green; agitate a part with carbon disulfid—this becomes amethyst-colored; another part with chloroform—this colors blue (compare results of the same Reagents under *Apomorphin hydrochlorid.*)

### **Apomorphin Hydrochlorid.**

$C^{17} H^{17} NO^2. HCl.$

Very seldom met, as it should be, as white, shining crystal-needles, but usually found as a gray or greenish-gray powder. Heated in a tube it changes to a green color and chars. Soluble in thirty (30) parts water at normal temperature; in forty (40) parts alcohol (0.83 sp. gr.); very sparingly in ether or chloroform. The watery solution is neutral and colorless, turns green on exposure to

air and light, more slowly if HCl is added. Ether removes the alkaloid from the green-colored watery solution, with a purple-red color—chloroform with a beautiful blue hue.

(a) Precipitates are obtained in the watery solution with Reagents 6, 12, 13 and 14 and with solutions of NaCl, KBr, KI, when containing not less than 0.10 molecule of the salt, expressed in gram, in a liter. All these precipitates turn green.

(b) Ammonia (Reagent 1) dissolves it with a brown color which turns reddish. In limewater it is soluble with a green color, afterwards changing into red and brown; very soon a greenish brown sediment settles down. In Reagent 6 it is soluble with a red color, also changing to green.

(c) The filtrate of the colorless watery solution turns green when shaken with peroxid of manganese; red, when peroxid of lead is taken,—in the latter case, however, the fluid becomes green too.

(d) Substituting barium peroxid, one obtains a green filtrate changing to a pink-red and brown color. Carbon disulfid, ether, or benzene, extract a constant purple or red color from all the above-named green fluids; with chloroform, a splendid blue solution is obtained. These red and blue colors are constant.

(e) Dissolve 0.005 g. Apomorphin hydrochlorid in two (2) c. c. acetic acid; the solution is colorless, but turns blood-red on shaking with a small crystal of  $\text{KIO}_3$  (Reagent 9); ether and chloroform extract an indigo blue color (alkaloid), and carbon disulfid extracts iodine with its usual amethyst color.

(f) A blue fluid is obtained in the course of an hour by agitating 0.050 g. Apomorphin hydrochlorid, 0.050 g. ferrous sulfate, and ten (10) c. c. water; the next day the fluid is blue-black, changing to dirty green. The blue fluid can be diluted with alcohol, but ether, benzene, chloroform, and carbon disulfid, remain colorless, when agitated therewith. N. B.—Ferrous sulfate does not affect Codein, Morphin, Narcein, or Narcotin.

(g) 0.001 g. Apomorphin hydrochlorid produces a mirror from reduced silver, in 0.5 c. c. of a  $\frac{N}{10}$  silver solution in the course of half a day; more quickly when ammonia water is added.

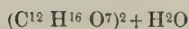
(h) Dissolve 0.075 g. potassium ferricyanid in two hundred (200) c. c. water; add one (1) c. c. ferric chlorid solution (Reagent 4); a drop or two of this mixture is added to a few crystals of Apo-



morphin hydrochlorid (porcelain lid of a crucible); a precipitate of Prussian blue forms immediately.

(i) 0.005 to 0.010 g. Apomorphin hydrochlorid, injected hypodermatically, causes vomiting in adults.

### Arbutin.



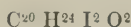
(THE GLUCOSID OF FOLIA UVÆ URSI.)

Crystallizes in needles. Melting point about  $166^\circ$ ; water free, it melts at  $144^\circ$ ; the melted mass solidifies colorless; when overheated, it chars and gives off an aromatic and a caramel odor. Soluble in eight (8) parts water at the normal temperature; in much less at  $100^\circ$ .—These solutions are neutral toward litmus and have a bitter taste; neither salts of the heavy metals nor tannin give a precipitate; neither are they affected by an alkaline cupric tartrate (Fehling's) solution, even at the temperature of boiling water; boiled with diluted sulfuric acid, however, they reduce the copper from cupric to cuprous oxid from the solution. Nearly insoluble in ether, chloroform and carbon disulfid; soluble in sixteen (16) parts alcohol (0.83 sp. gr.)

(a) Arbutin gives color reactions with acids; yellow changing to red-brown with  $\text{H}^2\text{SO}^4$ ; yellow with  $\text{HNO}^3$ ; a few mgr. evaporated with HCl leave hardly a colored residue.

(b) A mixture of 0.050 g. Arbutin and (1) g. peroxid of manganese, heated in a glass tube, gives off acid vapors to moist blue litmus paper, and likewise an odor of quinon.

(c) Dilute on a porcelain lid a drop ferric chlorid solution (Reagent 4) with water, until the peculiar yellow color of the Reagent can hardly be noticed, when the addition of Arbutin produces a light blue color.

**Aristol : Diiododithymol.\***

(Compare *Thymol*, page 146.)

An amorphous powder, of flesh color, nearly odorless and tasteless; does not affect litmus paper. Gelatinized starch solution does not give an iodine reaction when shaken with Diiododithymol and cold water; it fades in direct sunlight, seemingly without losing iodine. Heated in a glass tube, it decomposes, gives off iodine, and vapors that are acid to litmus paper.

Easily soluble in oil (olive oil) .1:10; chloroform and carbon disulfide dissolve it largely, with a yellow-red color; solubility much less in ether and alcohol; water and caustic soda solution do not moisten, and do not dissolve it, even at 100°.

(a) Strewn on sulfuric or nitric acid, Diiododithymol does not seem to change. A red solution is obtained when sodium nitrate ( $\text{Na NO}_3$ ) is added to the sulfuric acid; by substituting a *nitrite*, one obtains a blue colored fluid.

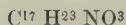
(b) Ferric chloride (Reagent 4) has no effect on an alcoholic solution of Diiododithymol; when the solution is evaporated to dryness on a water bath, however, it leaves a black residue, that is soluble, with dark brown color, in chloroform and in carbon disulfide, but insoluble in water.

(c) Carbon disulfide does not extract iodine from a filtrate of Diiododithymol when the latter has been strongly shaken with cold water, not even after the addition of bromine water; after the water is warmed, shaken again with Diiododithymol, and filtered, the result is colorless as before, but now carbon disulfide and bromine water show the presence of iodine in the cold filtrate.

(d) The presence of iodine can also be proved by a piece of moistened writing paper suspended in the vapor of hot water that is shaken with Diiododithymol.

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\*It is recommended to employ this second title exclusively.

**Atropin.**

Crystallizes in needles. Melting point of the dried salt  $115^{\circ}$ ; but it melts under boiling water. Soluble in ether, alcohol, chloroform and glycerol; very little in carbon disulfid. Atropin, placed on red litmus paper, moistened with alcohol, has hardly an alkaline reaction—none at all on phenolphthalein paper; it is distinctly alkaline to both reagents, however, when touched with a drop of water. The reddened phenolphthalein paper loses its color by drying, but reddens somewhat again when moistened anew, with water.

In a very dilute, watery solution (1:100.000) it dilates the pupil for a few hours. (This physiological test does not cause so much inconvenience as is commonly believed. One frequently and involuntarily undergoes it, when assaying belladonna leaves or root.)

(a) Hg O is thrown down when 0.001 g. Atropin is dissolved in one (1) c. c. alcohol (0.83 sp. gr.) and one (1) c. c. of a mercuric chlorid solution (27.10 g. Hg Cl<sup>2</sup> to one liter water) is added, the whole being warmed on a water-bath; when the Atropin is added afterwards, however, no such reaction takes place.

(b) Reagents 12 and 14 produce precipitates in a watery solution of Atropin, amorphous at first, but very soon taking on crystalline form. These forms are characteristic.\*

(c) Tannin produces, in watery solutions of Atropin, a precipitate, that is soluble in excess of the Reagent, and in acetic acid, but not in excess of the Atropin solution.

(d) Potassium dichromate (Reagent 17) gives no precipitate in said Atropin solution.

(e) Picric acid (Reagent 16) causes a precipitate only in Atropin solutions made with boiling water.

(f) A solution of iodine in potassium iodid (Reagent 7) gives a precipitate in an acidulated watery solution of Atropin.

(g) By boiling 0.10 g. Atropin with three (3) c. c. water and 0.20 g. calomel, the latter turns black; filter boiling hot, and supersaturate the alkaline fluid, decanted from the crystals that

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\*Artistic reproductions of the crystal forms of double salts of Atropin are found in T. G. Wormley's *Microchem. of Poisons*, 2d Edit. 1885, Philadelphia, J. B. Lippincott & Co.

form by cooling, with  $\text{HNO}_3$ ; add silver nitrate solution five (5) per cent; this gives a voluminous precipitate.

(h) Heat 0.001 g. Atropin in a small test tube until white vapors arise; add one (1) c. c. sulfuric acid (1.84 sp. gr.); heat a little longer, until the acid commences to color; add, along the sides of the tube, and at a safe distance from the operator, two (2) c. c. water, drop by drop; note the odor, suggestive of flowers. Repeat this reaction, but drop a small crystal  $\text{MnO}_4 \text{K}$  into the acid solution before the water is added; in this case an odor of bitter almonds will be observed. A trace  $\text{Cr}^{+6} \text{K}_2$  produces yet another odor. An aromatic odor is also obtained from the decomposition products of Atropin and  $\text{HCl}$  or  $\text{H}_3\text{PO}_4$  and even after boiling it repeatedly with water, evaporating, and redissolving the residue in hot water.

(i) Dissolve 0.001 g. Atropin in a drop  $\text{HNO}_3$ ; evaporate to dryness; prepare an alcoholic solution of  $\text{KOH}$  (1 g. : 5 c. c.); a drop of this solution, added along the side of the porcelain dish or lid, produces a violet color, when it comes in contact with the residue;—this test does not succeed in the presence of strychnine\* —(compare *Strychnine*, page 136).

Or triturate 0.001 g. Atropin and 0.001 g. sodium nitrate ( $\text{NaNO}_3$ ) together on a porcelain lid; add one (1) drop of sulfuric acid (1.84 sp. gr.) and spread the mixture out in a thin film; strew upon this 0.005 g. of coarsely powdered potassium hydrate ( $\text{KOH}$ ); finally add one (1) drop of alcohol of 0.83 sp. gr.

(j) Dissolve 0.010 g. Atropin in very dilute  $\text{HCl}$ ; warm this, add a five (5) per cent. gold chlorid solution, and set aside to cool. —Compare the crystal forms to Fig 2, Plate XIII. of Wormley's Atlas (Microchemistry of Poisons); Atropin gold chlorid solidifies to a granular mass. Collect the crystals, wash and dry and take a melting point determination.—Atropin gold chlorid double salt melt at  $137^\circ$ .

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\*Amer. J. o. Pharm., February, 1893, page 85.

**Atropin Sulfate.**

Melting point of the previously dried salt 180°. It crystallizes from an alcoholic solution in needles. Easily soluble in water; in 2.6 parts of alcohol; less so in ether, chloroform and carbon disulfid. Neutral to litmus paper.

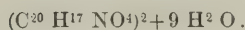
(a) Limewater does not produce turbidity in a watery solution (1:50); but such results are obtained by ammonia (Reagent 1), or sodium hydrate solution (Reagent 20).

(b) Picric acid (Reagent 16) gives a crystalline precipitate.

(c) Solutions of mercuric chlorid (Reagent 13) and potassium dichromate (Reagent 17) do not produce precipitates in the above named watery solution; neither a ten (10) per cent. Pt Cl<sup>4</sup> HCl solution in a solution of 1:100.

(d) Tannin gives a precipitate soluble in an excess of the reagent (Reagent 24).

(e) A boiling solution of Atropin sulfate does not decompose calomel; otherwise its reactions are the same as those of Atropin.

**Berberin.\***

Small bright yellow, or red-yellow (orange colored) needles, according to the process of manufacture. Melting point about 145°, whereby is produced a brown, amorphous mass. Soluble in water, at normal temperature, 1:300 parts, with a canary yellow or orange color; in alcohol and in amyl alcohol; not in ether, chloroform or carbon disulfid. These solutions do not affect litmus. When Berberin is manufactured from Berberin sulfate, its solutions absorb carbon dioxid from the atmosphere, but no such

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\* Compare Dr. R. Gaze U. Berberin and Hydroberberin in the Arch. der Pharm. 1890, page 604; Prof. E. Schmidt, U. Berberisalkaloide; Arch der Pharm. 1890, p. 596.



absorption takes place when it is made from Acetonberberin. Berberin is only soluble in chloroform when freshly precipitated.

In pharmacy, Berberin is chiefly substituted by its two principal salts, the hydrochlorid and the sulfate, both of which are highly yellow colored and bitter; the yellow color of a solution of the hydrochlorid is to be seen in a 1:1,000,000 dilution. This may be a test individual to the writer (J. B. N.).—[To verify it, dissolve 0.010 g. of Berberin hydrochlorid in one hundred (100) c. c. of water; call this solution "A." Dilute ten (10) c. c. of solution "A" to one hundred (100) c. c.—solution "B." [Swallow five (5) c. c. of the latter. To the writer [J. B. N.], solution "B" is faintly bitter (1:100,000)]. Dilute further ten (10) c. c. of "B" to one hundred (100) c. c.; a column of twenty-five (25) c. c. fluid in a twenty-five (25) c. c. graduate, is faintly yellow to me (1:1,000,000). The coloring power of Berberin is about the same.]

(a) Neither ammonia water (Reagent 1), lime water (Reagent 10), borax or caustic potash solutions have an effect upon paper colored yellow and dried with a solution of Berberin or a Berberin salt; turmeric paper turns red-brown when thus treated.

Berberin solutions give a permanent yellow color to paper when absorbed and dried.

(b) Crystals of Berberin nitrate begin to form on adding one (1) c. c. of nitric acid (Reagent 15) to three (3) c. c. of a watery solution of Berberin; the color of the mixture remains unaltered, but changes to brown-red when two (2) c. c. of the Berberin solution are taken; crystals form also. The mixture becomes dark-red, by mixing equal volumes of Berberin solution with nitric acid; but no crystals are formed now, however.

(c) Crystals of Berberin hydrochlorid and Berberin sulfate are formed when hydrochloric and sulfuric acids are added to a watery or alcoholic Berberin solution. They are easily prepared from fluid extract of Golden Seal in the following way: Ten (10) c. c. of fluid extract Golden Seal is poured into ninety (90) c. c. alcohol of ninety-four (94) per cent.; the sediment is, after a while, filtered off and two (2) c. c., respectively of hydrochloric or of sulfuric acid, added to fifty (50) c. c. of the clear filtrate; the acid mixture is then left to itself in a cool place for a few hours and the crystals that form, serve for all the reactions of Berberin, if washed with

a mixture of equal portions of alcohol ninety-four (94) per cent. and ether, and dried at a temperature of about 50°.

(d) Berberin and its salts give an olive green color reaction when warmed with sulfuric acid (Reagent 21);—sensitive 1:10,000. Add to the residue of evaporation of one (1) c. c. of solution “A,” one (1) drop of sulfuric acid; warm to about 75°; an intense olive-green color reaction, not changing to brownish-green as in “(g),” is obtained. The residue of one (1) c. c. of solution “B” gives too faint a reaction; too faint to be of value, nevertheless, it can be seen.

(e) A fragment of sodium nitrate ( $\text{NaNO}_3$ ), or of potassium dichromate (the first salt to be preferred, as it is colorless) added to a cold solution of Berberin (or of one of its salts) in sulfuric acid, (Reagent 21,) causes violet streaks to flow in the acid, when the mixture is stirred with a small glass rod; this reaction is sensitive to 1:10,000.

(f) Bromin water (Reagent 2) and Chlorin water (Reagent 3), the former less sensitive, however, give both a purple zone when added to a watery solution containing Berberin, diluted with an equal volume of sulfuric acid; this colored zone is permanent for a day. The reaction is sensitive with chlorin water, in a 1:250,000 of a g. as a limit, and distinctly in a 1:100,000 (0.00001). With bromin water, in a 1:10,000 g., as a limit. To verify this test, dilute one (1) c. c. of solution “B” with one (1) c. c. sulfuric acid, and add five (5) drops of chlorin water as top layer to the warm mixture; repeat the same reaction with bromin water. The zone with chlorin water, added to 1:250,000 g. is too delicate to be decisive.

(g) 0.020 g. of ammonium molybdate, triturated with five (5) drops of sulfuric acid, gives a green color reaction, changing immediately to brown-green, with 0.0001 (1:10,000) g. Berberin or one of its salts (residue of evaporation of one (1) c. c. of solution “A”.)

(h) Iodin water (Reagent 6) gives a greenish-red fluorescent precipitate in a solution of Berberin, or of a Berberin salt, containing 0.00001 g.; (1:100,000)—add five (5) c. c. of the reagent to ten (10) c. c. of solution “B;” this reaction does not succeed as beautifully in solutions stronger than the foregoing. One (1) drop of Reagent 7 added to ten (10) c. c. of the 1:100,000 solution gives a more reddish-brown than an iridescent red-green fluid; five (5) drops of Reagent 7 added to ten (10) c. c. of a 1:1000 solution of a

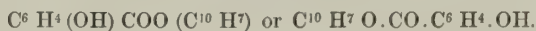
Berberin salt give a voluminous brown precipitate that soon changes to a dirty green.

(i) Berberin (and its salts) gives precipitates with the other general alkaloïdal reagents, to which, however, it is not very sensitive—*e. g.*, it is not sensitive in a 1:10,000 dilution to Reagents 4, 13 or 17; to Reagents 12, 16 and 24 it is sensitive in a 1:10,000 dilution.

(j) One (1) drop of yellow ammonium polysulfid,  $(\text{NH}_4)_2\text{S}(\text{NH}_4)\text{HS}$ , gives a flocculent red-brown precipitate in five (5) c. c. of a solution of 1:1,000 of Berberin and in like solutions of Berberin hydrochlorid and sulfate; a dark brown precipitate in more concentrated solutions, but no precipitate in a 1:5,000 dilution.

(k) Ten (10) c. c. of a solution of 0.010 g. Berberin in water, are discolored in a few hours when slightly warmed ( $50^\circ$ ) with ten (10) c. c. of diluted sulfuric acid (1.1 sp. gr.) and five (5) g. granulated zinc (zinc dust is preferable) until hydrogen develops quietly and steadily. By this action hydrogen is developed in its nascent state, and the Berberin is reduced to Hydroberberin,  $\text{C}^{20}\text{H}^{21}\text{NO}^+$ ; nitric acid restores a color reaction of red or yellow red in this fluid, but such is not positive evidence of the presence of Berberin. Turmeric root, rhubarb root, buckthorn or cascara sagrada bark, chrysarobin, etc., all give yellow percolates or filtrates, in which hydrogen in a nascent state destroys the color; but in these cases nitric acid does not always restore it. The zinc sulfate obtained by the development of hydrogen can be removed by the addition of alcohol to its concentrated solution; on filtering off, expel the alcohol on the water bath, dilute the residue with water, and add a solution of iodine in potassium iodid (Reagent 7); an amorphous precipitate of hydroberberin hydriodid, that is insoluble in water, is thrown down.

**Betol.—Naphthalol: Naphthosalol:  $\beta$ -Naphthyl-salicylate.**



Tasteless microscopical crystals that have usually an odor slightly suggestive of Salol—compare *Salol*, page 126. Melting point  $95^{\circ}$ ; heated in a glass tube it gives off irritating vapors of an acid reaction to moist litmus paper—partly Betol; then chars.

Is easily soluble in chloroform, carbon disulfid, and in ether; in alcohol only when the latter is warm; also in fatty oils 1:25; in water with difficulty even at  $100^{\circ}$ ; Betol crystallizes when the solution cools off. Does not act upon litmus paper.

(a) Betol thrown upon sulfuric acid (Reagent 21) colors the latter yellow, subsequently changing slowly to brown.

(b) Gives no color reaction with nitric acid, in the cold; at the boiling point a flocculent sediment or red drops are formed.

(c) A mixture of two (2) c. c. sulfuric acid (Reagent 21) 0.20 g. of Betol and 0.10 g. chloral hydrate has a brown-red color.

(d) By adding sodium nitrate ( $\text{NaNO}_3$ ) to the sulfuric acid test “(a)”, Betol produces a greenish-brown coloring; substituting sodium *nitrite* for the nitrate, the color is a more reddish brown, but by substituting nitric *acid* the sulfuric acid remains yellow.

(e) Betol added to Reagent 22, produces only a yellow color when warmed upon the water bath.

(f) Betol is insoluble in sodium hydrate solution (Reagent 20), even at the boiling point.

(g) Betol warmed with a little slacked lime and water gives a blue fluorescent filtrate; this remains clear, when slightly acidulated with hydrochloric acid; one (1) drop of ferric chlorid solution (Reagent 4) added to it, produces a violet color. One drop ferric chlorid solution (Reagent 4) gives the same color to five (5) c. c. of water that has been boiled for some time, with a few crystals of Betol; replacing the water that evaporates; the same Reagent colors an alcoholic solution of Betol brown, however. Betol triturated with Reagent 4 gives no coloring at all, not even by warming the mixture.

(h) 0.010 g. Betol gives a blue color reaction with two (2) c. c.

of sulfuric acid heated nearly to the boiling point; a yellow-green clear fluid is obtained by adding water to the same.

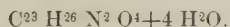
(i) Ammonia does not give the fluorescent reaction described under "(g)" when agitated with Betol, but it becomes yellow by warming. An unctuous dark brown sediment is obtained when the Betol is filtered off and the ammonical filtrate evaporated to about one-third; crystals of salicylic acid form in the cooling fluid.

### **Bromoform.**



Is a clear colorless liquid, of a sweet taste, a pleasant smell resembling chloroform somewhat, and coloring brown on contact with air and light. Sp. gr. as high as 2.834 at 0°, 2.775 at 15°, which is higher than in any other organic compound. Boiling point (normal condition) 152°. Soluble in ether, in alcohol, and in glycerol; slightly soluble in water. Melting point —8° solidifies at —9° to a crystalline mass.\*

### **Brucin.**



Dried at 105° to constant weight, it melts at 178°. It is readily soluble in alcohol; also in one hundred and fifty (150) parts boiling water, from which it crystallizes in needles. An aqueous saturated solution of Brucin (15°) contains about 1:1600 (solution "A"), and has an alkaline reaction to litmus paper; it is easily soluble in chloroform; less so in ether; slightly in ammonia; insoluble in fixed caustic alkalies. Is intensely bitter, even in 1:500,000 solution.

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\* Compare Squibb's Ephemeris, Vol. IV., No 1, 1893, page 15.



Dissolve 0.010 g. Brucin in one hundred (100) c. c. warm water; cool; make up to one hundred (100) and call this solution "B." Dilute ten (10) c. c. of "B" to one hundred (100), two hundred (200) c. c. and to three hundred (300), four hundred (400), five hundred (500) c. c. Call these solutions "C" and taste. Five (5) c. c. of "C" five hundred (500) are bitter to the writer [J. B. N.], when swallowed; this is the individual limit.

(a) In the watery solution "A", potassium dichromate (Reagent 17) does not give a precipitate; iodine solution (Reagent 6) only a slight turbidity; picric acid solution (Reagent 16), tannin solution (Reagent 24), and Reagent 12 give slight precipitates.

(b) Brucin imparts to chlorin water (Reagent 3), when agitated with it, a red color; this color is not permanent.

(c) A purple color, soon fading, forms if one (1) drop of Reagent 22 is spread out as a thin film and one (1) drop of Brucin solution "A" dropped on it, reappears with more Brucin solution.

(d) Brucin dissolves in diluted nitric acid, of not less than 1.05 sp. gr., with a blood-red color, permanent for days if the alkaloid is present in large excess; the red color fades to yellow when the solution is warmed to about 50° for ten minutes. In a 1:100,000 dilution, however, it shows the color reaction too faintly to afford positive evidence of the presence of the alkaloid; in a 1:50,000 it produces it admirably and accurately.—Evaporate one (1) c. c. of a mixture of ten (10) c. c. of solution "B" (0.010 g. in one hundred (100) c. c. and forty (40) c. c. water; add to the minimal residue a trace of sulfuric acid (Reagent 21) and a small drop of nitric acid (Reagent 15). Freshly prepared stannous chlorid solution (obtained by boiling tin foil in excess, with hydrochloric acid to nearly dry, renewing the acid and filtering through asbestos) changes the yellow color to violet.

(e) If 0.001 g. potassium dichromate is added to one (1) c. c. glacial acetic acid, 0.001 g. Brucin further added, and sulfuric acid (Reagent 21) dropped into the mixture, a color reaction similar to the nitric acid reaction is obtained.

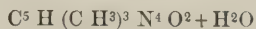
(f) Five (5) drops concentrated nitric acid decompose Brucin (0.005 g.) in the cold; the diluted (1.05 sp. gr.) acid—ten (10) c. c. being taken—at temperatures between 50° and 100°. The usual reagents for alkaloids (12, 16, 17 and 24) do not give a precipitate in this acid fluid; neither do caustic potash, or soda solutions.

(g) Brucin is also decomposed by mercurous nitrate (Millons' reagent).<sup>\*</sup> Spread one (1) drop of the reagent out to a thin film on a warm porcelain lid or dish, add 0.002 g. Brucin and five (5) drops of water; black  $\text{Hg}^2\text{O}$  is thereby formed; the Brucin is colored black too. Along the edges, the mixture becomes of a dirty violet or reddish yellow color, if slowly rotated.

(h) If reaction "(f)" is repeated, but instead of the other reagents, 0.005 g. sodium thiosulfate added to about ten (10) c. c. of the yellow diluted acid solution of Brucin, there is obtained a brown colored mixture, changing to a beautiful red and violet. Sodium thiosulfate does not change the yellow color of the acid after it is neutralized with calcium carbonate, but the colors reappear when more acid is added; hydrogen sulfid reproduces it also in the neutral fluid.

The yellow color of the decomposition products of Brucin and nitric acid is permanent. Sodium thiosulfate acts upon it even after weeks; but by repeatedly evaporating, and redissolving in water, it loses nitric acid, when sodium thiosulfate no longer gives the color reaction, save only after addition of an acid to the solution, acetic acid to be preferred.

### Caffein.



#### TRIMETHYLYXANTHIN.

Long flexible needles, melting at  $230.5^\circ$ ; and subliming at  $180^\circ$ . Boiling point  $384^\circ$ ; vapor odorless and condenses to crystals again without charring.

Soluble in seventy-five (75) parts water at  $15^\circ$ , in two (2) parts water at  $70^\circ$ ; in fifty-two (52) parts absolute alcohol; in eight (8) parts chloroform; sparingly in ether and in carbon disulfid. The saturated watery solution ( $15^\circ$ ) has a bitter taste but no action on litmus. Reagents 5, 15 and 21 do not visibly change it.

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<sup>\*</sup>Millons' reagent is prepared by adding mercury in excess to nitric acid of 1.2 sp. gr. and warming after the action has ceased.

(a) Its neutral or acidulated aqueous solution is not affected by Reagents 6, 7, 12, 16, 17 and 19.

(b) Reagents 11, 13 and 14 give a crystalline precipitate—immediately with the Reagents 13 and 14; after an hour with Reagent 11.

(c) A few c. c. of a tannin solution (Reagent 24) gives an abundant precipitate in one (1) c. c. of a Caffein solution; soluble in excess of the reagent. A mixture of one (1) drop of a Caffein solution and forty (40) drops of the tannin solution (Reagent 24) is clear.

(d) A few drops of a Caffein solution added to Reagent 22 become green after many hours.

(e) To an almost invisible residue of an evaporation of a pure caffein solution (identity reaction for a fl. extr. of kola nuts, guarana, coffee or tea) add a few drops hydrochloric acid and a minute crystal of  $\text{KCl O}_3$ ; evaporate to dryness; cool; expose to vapors of  $\text{NH}_3$ , when a purple color will be produced.

(f) To a similar residue as under “(e)” add a little bromin water (Reagent 2); evaporate to dryness; then add ammonia water, when a purple color also will be obtained.—Murexoin reaction.

(g) To one (1) c. c. acetic acid (1.064 sp. gr.) add 0.001 g. Caffein and 0.001 g. potassium bromate ( $\text{K Br O}_3$ ); heat to boiling point.—It remains colorless. Evaporated to dryness, the mixture leaves a dark red crystalline residue; heated carefully over the flame, the color becomes more intensely red.—Tetramethylalloxantin reaction.

### Cantharidin.



Cantharidin crystallizes from chloroform in laminæ. Melting point  $218^\circ$ ; heated higher, it gives off a heavy, white vapor, condensing unaltered to crystals. Easily soluble in acetone, sulfuric acid and glacial acetic acid; less so in chloroform (1:80); very little in 90 per cent. alcohol; benzene 1:500; ether, 1:1,000; nearly insoluble in carbon disulfid; water, 1:5,000;—the aqueous solution is nearly

tasteless, but by no means devoid of vesicatory power even if taken in small quantities; it is soluble in fatty oils.\* It has an acid reaction to very sensitive litmus paper; is volatile at 100°.

(a) The most important reaction is its vesicating power. Dissolve 0.001 g. Cantharidin in alcohol, or in an oil, and apply the solution with a camel's hair brush on the soft part of the upper arm or behind the ear. This is a painless experiment, one that causes very little inconvenience, and must be taken where positive proof is lacking of the presence of it.

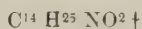
(b) It slowly changes Reagent 22 to a green-colored fluid.

(c) Barium water gives a crystalline precipitate in a watery (100°) solution, soluble in acetic acid.

(d) Subacetate of lead gives a slight turbidity.

(e) It combines readily with alkalies to form soluble salts. If nitric acid is added in slight excess to a solution of the soda salt, crystals of Cantharidin are thrown down.

### Carpain.



Carpain forms large colorless crystals, melting at 120°; slightly soluble in water, at 20°; 0.025 g. Carpain, agitated twenty-four (24) hours in a laboratory shaker (see Ph. Jour. and Transactions, March, '92, page 730), with fifty (50) c. c. of water, gives a filtrate, that is *very* bitter to the writer [J. B. N.] when two (2) c. c. are swallowed. This is alkaline to red litmus paper, and to cocconella tincture, but not to phenolphthalein.

It is very easily soluble in chloroform; easily in absolute alcohol, amyl alcohol and benzene; much less in ether and in ligroin.

(a) Bromin water (Reagent 2) gives a strong turbidity in the cold saturated watery solution.

\* See an extensive list on the solubility of Cantharidin in various menstrua, on page 19 of the Helfenberger Annalen, 1889. Berlin. Julius Springer.

† Dr. J. J. L. Van Ryn. Ned. Tydsch. voor Pharmacie, etc., April, page 102. s'Hage; van Cleef: 1893.

(b) Iodin water (Reagent 6) is not sensitive to Carpain in this dilution.

(c) Iodin in potassium iodid (Reagent 7), gives a heavy precipitate.

(d) Tannin solution (Reagent 4) gives a dense turbidity (slight precipitate).

(e) Mercuric potassium iodid solution (Reagent 12) gives a heavy precipitate.

(f) Carpain is not sensitive to potassium ferrocyanid solution (Reagent 19) in this cold watery solution.

(g) Neither is it sensitive to a five (5) per cent potassium chromate solution.

(h) Trinitrophenol (Reagent 16) gives a precipitate in its watery solution.

(i) Not sensitive to potassium dichromate (Reagent 17) in this dilution.

(j) Nor to mercuric chlorid (Reagent 13).

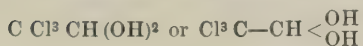
(k) It does not give a color reaction with hydrochloric, nitric, or sulfuric acid—neither with the pure acids, or with sulfuric containing nitric acid, or a trace  $\text{Fe}^2 \text{Cl}^6$ ; nor with ammonium molybdate dissolved in sulfuric acid, in the proportion given under article *Morphin*.

(l) A small particle of a crystal dissolved in Reagent 22, gives at first a dirty, not very well defined color reaction, which develops slowly into a *delicate*, clear, bluish grass-green color, permanent for more than an hour.

(m) A small particle of Carpain dissolved in Reagent 23, gives a *delicate* lilac color, lasting for more than an hour, and fading entirely to a colorless fluid.

(n) Its solution in carbon disulfid slowly colors yellow.



**Chloral Hydrate.**

Forms crystals (monoclinic prisms) melting at  $57^\circ$ ; decomposes at  $97.5^\circ$  into chloral ( $\text{CCl}^3 \text{CHO}$ ) and water; the vapor is not combustible. It has a pungent, irritating odor; is easily soluble in water at  $15^\circ$  (4:1) absorbing heat thereby, in other words, lowering the temperature of the water. An aqueous solution is without reaction to litmus, but has a disagreeable, sharp taste, not any more in large dilutions, *e. g.* four (4) g. to the liter of water. Soluble in alcohol, ether, volatile and fatty oils, liquid hydrocarbons, chloroform (1:5)—less soluble when the chloroform is strictly pure; in carbon disulfid (1:4), in closed tubes. In fact there seems to be no fluid in which Chloral hydrate is insoluble.

(a) Camphor, phenol, thymol and menthol all liquefy when triturated with Chloral hydrate in equal parts.

(b) Crystals of Chloral hydrate sink in sulfuric acid, but soon rise to the surface, however, and liquefy, decomposing into a turbid, colorless top layer of metachloral and Chloral.

(c) Litmus gives an acid reaction, and silver nitrate solution, five (5) per cent, a voluminous precipitate, in water boiled with a small lump of zinc and a trace of Chloral hydrate. Silver nitrate solution produces only a slight turbidity in freshly prepared watery or alcoholic solutions of Chloral hydrate.

(d) A solution of 0.020 g. Chloral hydrate, 0.030 g. resorcinol, and five (5) drops caustic soda solution (Reagent 20), has an intense red color, changing to brown-red; this solution has a yellowish-green fluorescence when diluted with one hundred (100) c. c. water—acids destroy the fluorescence. When 0.010 g. resorcinol is taken instead, the color is mere pink and fades slowly to greenish-yellow. By substituting lime water for the caustic soda solution, the fluid is lilac at first, but finally turns to a yellowish-green.

(e) If equal parts Chloral hydrate, resorcinol, and slacked lime, are triturated together, a white powder is obtained that soon becomes red (intense red when moistened) and finally turns brown. When thymol is substituted for resorcinol a beautiful violet powder is obtained.

30 *Chloral Hydrate.—Chloral Formamid.—Chrysarobin.*

(f) If 0.010 g. Chloral hydrate be dissolved in one (1) c. c. caustic soda solution (Reagent 20), a turbid fluid is obtained, soon giving off the odor of chloroform, the latter falling to the bottom in small drops.

(g) The turbid fluid under “(f)” will give the isonitril reaction, when agitated with three (3) drops of anilin. Compare *Acetanilid*, page 1.

**Chloral Formamid.**



TRICHLORALDEHYDIFORMAMID.

Colorless, odorless crystals, that are decomposed into chloral and formamid, when heated with water to 60°. Melting point, 114°. Heated with caustic soda solution (Reagent 20), an odor of chloroform and ammonia is perceived, the latter also recognized by its reaction to give white clouds from a glass rod moistened with hydrochloric acid.

A watery solution tastes bitter.

**Chrysarobin.**



Yellow, microscopical crystals, or a yellow amorphous powder; tasteless. Melts at 178° to a dark brown non-crystalline mass; chars at a higher temperature. Soluble in benzene, chloroform and glacial acetic acid; less so in ether and in alcohol.

(a) Caustic soda solution changes the yellow color of the opalescent filtrate of Chrysarobin, when this has been boiled with water, to red; this watery solution is neutral.

(b) Ferric chlorid (Reagent 4) produces in the alcoholic solution a dirty green-brown color.

(c) Caustic potash and soda dissolve Chrysarobin with a red color, which gives a green fluorescent fluid when diluted with water or alcohol.

(d) 0.010 g. Chrysarobin shaken with fifty (50) c. c. lime water gives to the latter a violet-red color.

(e) With ammonia (Reagent 1) the color is more of a brown-red; warming increases the color.

(f) Sulfuric acid immediately dissolves Chrysarobin with a yellow-red color; nitric acid slowly, with a faint yellow color.

(g) The following is the most characteristic reaction of Chrysarobin: Triturate 0.005 g. Chrysarobin and 0.005 g. sodium nitrate ( $\text{Na NO}_3$ ) with a glass rod barely moistened by means of a bit of damp cloth or paper, so that the mixture of Chrysarobin and sodium nitrate will remain nearly dry. Spread the mixture as thinly as possible on a porcelain lid with a glass rod to which only a trace of sulfuric acid clings. Strew on this layer a few small particles of solid caustic potash or soda; a black or dark violet zone forms around each, as moisture is attracted from the atmosphere, until soon the particles ( $\text{KOH}$  or  $\text{NaOH}$ ) are so many black drops. This color test is less characteristic when the layer is moistened with a glass rod dipped in caustic potash or soda solution. The layer becomes violet when ammonia is substituted for a solution of the fixed alkalies.

Goa powder is a crude Chrysarobin.\*

### **Cinchonidin Sulfate.**



Heated in a glass tube, Cinchonidin sulfate yields a beautiful red-colored tar. This test can be made use of to distinguish Peruvian from any other bark; only Cinchona alkaloids give this reaction.†

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\* Maisch, *Org. Mat. Med.*, 5th Ed., 1892, page 414. Phila., Lea Bros & Co.

† The conditions for this test are to be found on page 363 in Flückiger and Hanbury *Pharmacographia*; 2d Edition, London, 1879, McMillan & Co; more completely in Flückiger's *Pharmacognosie*, 3d edition, page 569; Berlin, 1891.

Soluble in about one hundred (100) parts water; less so in chloroform or alcohol; the watery solution has no fluorescence; gives no thalleioquin reaction. From a saturated watery solution Cinchonidin sulfate crystallizes in long, white needles, if four (4) times its volume of a saturated aqueous solution of phenol is added.

(a) One (1) c. c. of a five (5) per cent. potassium iodid solution gives a dense turbidity in one (1) c. c. of a watery solution of Cinchonidin sulfate; this turbidity disappears when two (2) c. c. water are added. Compare *Quinin sulfate* "(i)", page 112.

(b) Cinchonidin sulfate gives a similar compound of a *yellow* color, if treated according to the Herapathit test, described for quinin sulfate, composed of microscopically fine needles, turning brown only when dry.

(c) A precipitate is obtained when lime water (Reagent 10) is added to one (1) c. c. of the cold saturated solution of Cinchonidin sulfate, but it dissolves again when a total amount of thirteen (13) c. c. lime water is added.

(d) Dissolve 0.50 g. of the salt in twenty (20) c. c. water, by slightly warming; add 1.50 g. finely pulverized Rochelle salt (potas. et sod. tartras); dissolve and cool. Hereby is obtained a sparingly soluble (1:1200) crystalline precipitate of Cinchonidin tartrate.

(e) Dissolve 0.010 g. Cinchonidin sulfate in ten (10) c. c. water; solution ("A"). The precipitate caused by adding ammonia water (Reagent 1) q. s. to five (5) c. c. of this solution (0.005 g. of the salt) does not dissolve in fifty (50) c. c. ammonia water. To the other five (5) c. c. of "A" add ammonia water q. s. to obtain a precipitate; add five (5) c. c. ether; agitate strongly, when the precipitate immediately dissolves.\*

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\* In Prescott's Organic Analysis (N. Y., Van Nostrand, 1887) will be found, on page 141, interesting figures on the solubility of Cinchonidin, Cinchonin, Quinin and Quinidin in Ammonia water, by E. A. Ruddiman.

**Cinchonin Sulfate.**

Yields a red tar when heated in a glass tube. One (1) part of the water-free salt is soluble in ninety (90) parts of water at 20°, which solution is not fluorescent; it is much more readily soluble in alcohol; insoluble in ether. Deprived of its water of crystallization, it is soluble in sixty (60) parts chloroform, in the cold. It does not give a thalleioquin reaction.

(a) A saturated watery phenol solution causes a strong turbidity in a saturated watery solution of Cinchonin sulfate.

(b) The reaction with potassium iodid does not differ from the one described for *Cinchonidin* sulfate.

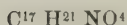
(c) Cinchonin salts do not give Herapathit-like compounds. Compare “(g)”, Quinin sulfate.

(d) Neither do they give a clear solution with an excess of lime water, as described for *Cinchonidin* salts; “(e)” page 32.

(e) If chlorin water (Reagent 3) is poured on some Cinchonin sulfate, this colors faintly yellow only, in the course of a day; the reaction takes place much quicker with Cinchonidin, Quinidin, Quinin, or the salts thereof.

(f) Dissolve 0.010 g. Cinchonin hydrochlorid or sulfate in ten (10) c. c. water; solution (“A”). The precipitate caused by q. s. ammonia (Reagent 1) added to five (5) c. c. (=0.005 g. of the salt) of this solution is not dissolved, even by adding as much as fifty (50) c. c. of the reagent. To other five (5) c. c. of solution “A” add q. s. ammonia to obtain a precipitate; add ten (10) c. c. ether and agitate strongly. The precipitate does not go into solution.



**Cocain.**

Cocain crystallizes in four to six-sided prisms of the monoclinic system. Melting point  $98^{\circ}$ ; in water  $85^{\circ}$ ; sublime at a higher temperature, partially decomposing. Strictly pure Cocain is odorless. It produces a blue spot if strewn on red litmus paper previously moistened with water or alcohol, which nearly disappears when the paper dries.

Cocain is easily soluble in ether, alcohol, benzene, chloroform and carbon disulfid; less soluble in water—at  $15^{\circ}$ , 1:1,500; at  $18^{\circ}$ , 1:1,370; at  $100^{\circ}$ , 1:600; soluble in fixed and volatile oils. Watery solutions have a strong alkaline reaction to methyl orange, but not to phenolphthalein. Cocain produces mydriasis, numbness of the tongue, blanching of conjunctiva of the eye, and has a slightly bitter taste.

(a) If Cocain is boiled with water and calomel, the latter blackens. This reaction does not take place in the cold (compare Cocain hydrochlorid) nor when alcohol is substituted for water.

(b) While Reagents 2, 6, 7, 12 and 24 produce a precipitate or a turbidity in a watery solution, Reagents 13, 16 and 17 do not visibly affect the same.

(c) An aromatic odor is developed if 0.020 g. Cocain is warmed on the water bath with two (2) drops sulfuric acid; benzoic acid sublimes along the sides of the tube; benzoic acid also forms by cooling, if 0.5 c. c. water is added at the beginning of the reaction. Crystals of benzoic acid are formed in the filtrate if more Cocain is taken, more sulfuric acid consequently added, the mixture also diluted with water, boiled with calcium carbonate, and filtered boiling hot; evaporate to a minimum, acidulate with hydrochloric acid, and allow fluid to cool.

**Cocain Hydrochlorid.**

Cocain hydrochlorid appears in prismatic crystals, when crystallized from an alcoholic solution. Melting point 200-202°\* when the liquid gives off a fruit-like odor; it turns brown if heated higher. Soluble in half its weight of water, the solution being without reaction to litmus, is bitter, inducing a feeling of numbness to the tongue; applied to the eye it causes dilation of the pupil. —[N.B. This test should not be made in stronger solution than four (4) per cent.] It is also soluble in four (4) parts of alcohol, chloroform, or amyl alcohol; insoluble in ethyl ether.

(a) Lime water gives a turbidity in the watery solution (1:50) which is redissolved when about ten (10) c. c. of the Reagent is added. Less ammonia water (Reagent 1) is required to redissolve the turbidity in a Cocain hydrochlorid solution, but the Cocain soon crystallizes, and more quickly than in the lime water test.

(b) 0.10 g. Cocain hydrochlorid dissolves without color in one (1) c. c. sulfuric acid, but the solution turns brown when heated; colorless crystals of benzoic acid sublime from it along the sides of the test tube.

(c) When Cocain hydrochlorid is triturated with an equal part of calomel, the mixture blackens by the slightest humidity (breathing upon it) or by moistening with alcohol. (Compare *Pilocarpin*, page 98.)

(d) Cocain hydrochlorid does not reduce potassium permanganate. One (1) drop of a 1:1000  $\text{KMnO}^4$  solution, added to five (5) c. c. of an acidulated watery solution of the salt, four (4) per cent., remains pink from one-half to one hour.

(e) 0.10 g. Cocain hydrochlorid changes the color of one (1) c. c. of Reagent 22 to red, when strewn upon it; the change to green (owing to formation of chromium sulfate) does not commence under an hour.

(f) A faint yellow fluid is obtained, which becomes red by

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\* This requirement is liable to be misinterpreted, inasmuch as many samples of Cocain hydrochlorid (sold as strictly pure by different respectable manufacturers), notwithstanding they satisfy requirement ("d") and are perfectly dry, are found to melt from 180° to 185°. The Cocain hydrochlorid, with low melting point, is acid towards litmus, in a two (2) per cent. watery solution. —(J. B. N.)

boiling, when one (1) drop ferric chlorid solution (Reagent 4) is added to a solution of 0.020 g. Cocain hydrochlorid in two (2) c. c. water.—Cocain alkaloid gives the same reaction. This red compound (benzoate of iron) is insoluble in ether and chloroform, but soluble in alcohol; the red colored fluid becomes yellow on addition of hydrochloric acid. Comparative tests must be made in this color reaction, by boiling a very dilute solution of ferric chlorid without addition of the Cocain hydrochlorid, and comparing the color changes with each other, because a hardly yellow colored solution of  $\text{Fe}^2 \text{Cl}^6$  becomes reddish colored by boiling.

(g) Another comparative test is as follows: Add one (1) drop ferric chlorid solution to a weak, watery solution of benzoate of soda; this gives a flesh-colored precipitate; dissolve the precipitate (benzoate of iron) in an excess of ferric chlorid. Compare the color of the fluid now obtained, with the Cocain reaction made above.

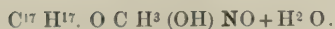
(h) Reagents 6, 12, 13, 14 and 16 give precipitates in dilute watery solutions of Cocain hydrochlorid.

(i) Reagents 11, 17, 19 and a 5 per cent.  $\text{K}^2 \text{Cr O}^4$  solution do not give precipitates in a watery Cocain solution, but crystals form in course of a day, after the addition of the two latter reagents. Cocain picrate (Reagent 16) crystallizes sooner.

(j) Two (2) drops of a tannin solution (Reagent 24) added to one (1) c. c. of a watery 1:50 solution of Cocain hydrochlorid causes a turbidity, that redissolves in an excess of the Reagent;—0.5 c. c.

(k) A green colored fluid is obtained when one (1) c. c. sulfuric acid is heated with 0.010 g. Cocain hydrochlorid until vapors are seen, and 0.020 g.  $\text{KIO}^3$  is now dropped into the warm solution; the fluid changes to a red-brown color, if over-heated. This is in reality a benzoic acid reaction, the acid being derived from the Cocain as a decomposition product; the acid itself produces a similar color test.

(l) Evaporate to dryness on a water bath, a solution of 0.010 g. Cocain hydrochlorid or Cocain alkaloid, in one (1) c. c. nitric acid; the residue is colorless. Add to it a few particles of caustic potash or soda and a few drops of alcohol, when a delicious and very permanent odor of benzoic-ethylester is developed.

**Codein.**

Codein forms octohedra, if crystallized from a watery solution. The anhydrous crystals have a melting point of  $150^{\circ}$ , and solidify unchanged on cooling; if heated higher, Codein turns dark green, changing to brown. Soluble in eighty (80) parts water at  $15^{\circ}$ , in seventeen (17) parts at  $100^{\circ}$ —an excess of Codein forms oily drops in boiling water, but crystallizes on cooling; the watery solution has an alkaline reaction to litmus paper, and is slightly bitter, is soluble in ammonia water.

Codein is easily soluble in ether, alcohol, benzene, chloroform, and carbon disulfid—in the latter menstruum even when it contains its water of crystallization; insoluble in liquid paraffin (petroleum ether).

(a) Iodin solution (Reagent 6) causes a turbidity in a watery solution (1:80) soon clearing up, but reappearing on addition of more of the reagent. Bromin water (Reagent 2) gives like results.

(b) Reagents 12, 13, 14, 16 and 24 give heavy precipitates in the Codein solution; the Reagents 11, 17 and 19 do not; crystals form, however, in course of a day, after the addition of Reagent 17.

(c) Codein does not give a precipitate in an alum solution notwithstanding its alkaline reaction, neither in solutions of magnesium or copper salts; but a saturated watery solution precipitates in five (5) per cent. zinc sulfate, iron sulfate, or manganese sulfate solutions—the hydroxides completely.

(d) Ferric hydroxid is precipitated from a ferric chlorid solution, when warmed on the water bath with a sufficient quantity of Codein, and a part of the ferric compound is reduced to a ferrous salt, as shown by the precipitation of Prussian blue on the addition of freshly-prepared five (5) per cent. potassium ferrieyanid solution to the filtrate.

(e) Codein assumes a brown color when treated with the mixture of  $\text{Fe}^2 \text{Cl}^6$  and  $\text{K}^3 \text{Fe} 6 \text{CN}$ , as described in chapter upon *Morphin* (g). The fluid turns to a dirty green.

(f) 0.050 g. Codein colors red, when strewn upon two (2) c. c. nitric acid; the acid itself becomes yellow-colored, only when warmed.



(g) Concentrated sulfuric acid (Reagent 21) dissolves Codein, colorless, even when warmed five minutes with the acid on the water bath—the test tube must have been previously rinsed with the acid for this reaction. Frequently the reaction fails and the acid turns somewhat green. The acid solution becomes immediately green, blue and violet, when touched yet warm with a very dilute solution of ferric chloride on a very small glass rod, and kept warm on the water bath for a little while. One (1) drop of ferric chlorid (Reagent 4) is therefore diluted with three (3) c. c. water. Water or alcohol discolors the blue Codein solution thus obtained; chloroform does not affect it.

(h) The solution of Codein in sulfuric acid becomes green, changing to dark violet, when stirred with a glass rod of the size of a match, slightly moistened with a trace of nitric acid (Reagent 15).

(i) A mixture of Codein and sodium nitrate ( $\text{NaNO}_3$ ) strewn on sulfuric acid gives a brownish-black coloration, changing to green and red-brown.

(j) Codein remains colorless when agitated with weak chlorin water, Reagent 3 diluted half; strong chlorin water gives a beautiful red color, especially when ammonia water (Reagent 1) is added.

(k) Diluted sulfuric acid (1.11 sp. gr.) warmed with Codein on a water bath, becomes pink-colored.

(l) Codein does not separate iodine from a  $\text{KIO}_3$  solution, neither in the cold nor by warming, as morphine does; only after many days contact at the temperature of the water bath.

(m) Codein gives with the tungstates only very faint blue color reactions, which soon fade when treated as described under reaction “(d)”, article *Morphine*, page 75. Bismuth, titanium and molybdenum salts act similarly, but much less intensely than with morphine.

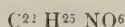
(n) A not too small particle of iodine, dropped into the watery Codein solution, does not become surrounded with fine crystalline needles; a distinction from *Narcein*.—See page 83, “(h)”.

(o) Codein leaves a dark brick-red colored mass when a crystal thereof is dissolved in nitric acid; the solution evaporated to dryness and a little of a solution of KOH in absolute alcohol (1:10) poured over it, and the mixture is evaporated to dry again.



**Codein Phosphate.**

Appears as colorless crystalline needles, soluble in two (2) parts of water, less so in alcohol—these solutions have an acid reaction toward litmus, and taste bitter. Soluble in weak chlorin water without visible change; ammonia water darkens this solution a little, and strong chlorin water gives a beautiful red coloring. Dissolved in sulfuric acid it gives the same reactions to  $Fe^2 Cl^4$ , to molybdic acid, to bismuth subnitrate, titanio acid and tungstates, as Codein. Melts to a yellow mass, when heated.

**Colchicin.**

or



A yellowish amorph powder.

Soluble in cold water, less so in warm; also in alcohol; hardly soluble in ether. These solutions are citron yellow, very bitter, and have no reaction to litmus; an addition of a mineral acid increases the intensity of the yellow color. A fairly pure Colchicin for all the following reactions is obtained by expelling the alcohol from five (5) c. c. of a standardized (0.5 per cent. alkaloid) fluid extract colchicum seed, then cooling, adding (5) c. c. of cold water to the residue, stirring a while, and filtering. This brownish-yellow solution ("A") has an acid reaction towards sensitive litmus paper; turns yellow when to one (1) drop of this solution one (1) drop of ten (10) per cent.  $H^2 SO^4$  is added.

(a) Reagent 12 does not give a precipitate (only a turbidity) in the proportion of one (1) c. c. of the watery filtrate, diluted with one (1) c. c. water, and two (2) drops of the Reagent; one (1) drop of the Reagent throws down, however, a heavy precipitate in one (1) c. c. of the watery filtrate of the same dilution, when acidulated with  $H^2 SO^4$ . This precipitate is soluble in a large excess,—ten (10) to fifteen (15) c. c.—of the reagent. It is also easily soluble

in alcohol, but does not form crystals\* when the alcohol evaporates. Reagent 12 can be diluted ten times for this reaction.

(b) A watery solution of crude Colchicin "A" reduces alkaline cupric tartrate solution (Fehling's fluid) in a few hours, in the cold, by mixing the two in equal proportions. Colchicum seed contains a considerable amount of sugar.

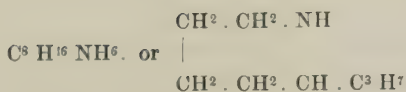
(c) Evaporate one-half (0.5) c. c. of solution "A" by rotating over a large surface in a warm, evaporating dish. (1) A few drops of a ten-times diluted ferric chlorid solution (Reagent 4) added to the brown-yellow film, previously moistened with one-half (0.5) c. c. alcohol, produces a greenish-brown coloring. (2) Sulfuric acid (Reagent 21) colors the film bright yellow. (3) Violet streaks, soon fading to brown, are obtained by touching the sulfuric acid with a small glass rod moistened with a trace of nitric acid (Reagent 15). (4) Nitric acid of 1.4 sp. gr. alone, gives the same violet color-reaction. Evaporate as under "(c)" two (2) drops of solution "A" diluted with five (5) drops of water, in order to obtain a minimum quantity of Colchicin, and spread out inside a warm dish.—N. B. Where Colchicin is separated in a toxicological case, it has been found (Arch. der Pharmacie, '89, page 404) NOT TO GIVE as sharp a reaction with  $\text{HNO}_3$ , as the alkaloid isolated from the seeds, gives. (5) If one (1) c. c. of alcohol is added to the Colchicin in the dish, after the treatment with nitric acid, with or without sulfuric acid, there is obtained a brown liquid, changing to a bright red, when dropped into three (3) c. c. of ammonia water (Reagent 1). Neither ether or chloroform extract the color from the red fluid, but it fades on evaporation; ammonia restores the red color when alcohol is added to the residue of evaporation, decanted from the nitrate and sulfate respectively.

(d) A strong watery solution of pure phenol gives, with a watery Colchicin solution, a white precipitate, turning bright yellow. To make use of solution "A" for this reaction, extract the Colchicin from one (1) c. c. of the watery solution with ether, decant, evaporate, and redissolve the ethereal residue in one (1) c. c. of water.

(e) Five (5) c. c. Chlorin water (Reagent 3), give a yellow precipitate in one-half (0.5) c. c. of solution "A," soluble in ammonia water with an orange color.\*

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\* Fasbender and Schoepp published very interesting analytical results of their research on an alkaloid in beer, possessing many identity reactions similar to those of Colchicin. Compare Bull. o. Pharmacy, vol. vi., 1892, page 622.

**Coniin.**

Coniin is a colorless fluid at the normal temperature; has a melting point of  $-2.5^\circ$ ; boiling point  $166^\circ$ ; sp. gr. 0.862 at  $0^\circ$ ; a characteristic repulsive odor and taste, suggestive of tobacco. When Coniin vapors are diluted with moist air an odor suggestive of mice is developed; a mousey smell is perceptible in large dilutions. Soluble in acetone, ether and alcohol; not in all proportions with benzene, petroleum ether and chloroform; it dissolves clear in water (1:150) at  $15^\circ$ , and becomes turbid under the warmth of the hands, only to clear up again on cooling. It burns from a glass rod in the flame with a bluish tinge, without charring.

(a) The watery solution has an alkaline reaction towards litmus—and phenolphthalein paper.—The reaction toward the latter is probably due to a trace of ammonia usually present. 0.050 g. of calomel blackens, therefore, when shaken with five (5) c. c. of the Coniin solution and  $\text{HgCl}^2$  can be detected in the filtrate, with  $\text{H}^2 \text{S}$ , by its peculiar colored precipitate.

(b) Add to ten (10) drops of ether in a shallow glass crystallizing dish two (2) drops of Coniin and cover with filter paper; set upon the paper a common-sized watch crystal containing bromin water (Reagent 2); invert a beaker over the whole arrangement. Needle-shaped crystals of Coniin hydrobromid soon form in the dish, as well as next to the watch crystal—see *Nicotin*, page 85. Coniin hydrochlorid is formed, if hydrochloric acid is substituted for the bromin water. Both are easily soluble in alcohol and water. If a watery solution of these Coniin salts is shaken with  $\text{MgO}$ , and next with  $\text{CS}^2$ , the latter turns yellow. The crystals of these salts possess the power of double refraction, and exhibit the well-known beautiful array of colors in polarized light under the microscope <sup>290</sup>.

(c) Reagents 2, 6, 7, 11, 12, 13, 14, 16 and 24, but not Reagents 17 and 19, give in the watery Coniin solution amorphous precipitates, often appearing as oily drops.

(d) Ten (10) drops of a watery Coniin solution—ten (10) drops to twenty (20) c. c. water—give precipitates of  $\text{Al}^3 (\text{OH})^3$  in five (5) c. c. of a five (5) per cent. alum solution; of  $\text{Fe}^3 (\text{OH})^3$  in five (5) c. c. of a five (5) per cent. ferric chlorid solution; of  $\text{MgOH}^2$  in five (5) c. c. of a five (5) per cent. magnesium sulfate solution and of  $\text{CuOH}^2$  in five (5) c. c. of a copper sulfate solution, 1:500.

(e) A blue precipitate is formed when one (1) drop of a ten (10) per cent. copper sulfate solution is dropped into five (5) drops of the watery solution of Coniin, “(d)”, if a narrow test tube is used; the fluid itself is colorless, or at most with a bluish tinge, in so far as the Coniin does not contain more than a trace  $\text{NH}^3$ ; but if it contain more  $\text{NH}^3$ , the blue color of the fluid will be distinctly seen by taking a watery solution of  $\text{Cu SO}^4$ , 1:2000.

(f) Carbon disulfid colors yellow, when shaken with the watery Coniin solution 1:150. The watery fluid, when separated from the  $\text{CS}^2$ , gives a brown precipitate in solutions of copper sulfate; colors a dilute ferric chlorid solution dark red-brown; and gives a milky opalescence in dilute acids.—These reactions are evidences of the presence of a thiosulfate and a sulfite.

(g) Considerable heat is developed from the mutual action of five (5) drops Coniin upon five (5) drops carbon disulfid; the latter becomes yellow-colored and thiosulfate (separation of finely divided sulfur, with its peculiar refraction properties) can be detected in water when agitated with the mixture.

(h) Coniin dissolves sulfur. If 0.020 g. sulfur is moistened with Coniin, it softens and colors red; water extracts a thiosulfate again.

(i) Crystals of Coniin hydrochlorid form when ten (10) drops Coniin are shaken with 0.050 g. calcium chlorid ( $\text{CaCl}^2$ ) and one (1) c. c. alcohol, and the alcohol evaporates spontaneously.

N.B. A ptomain has been isolated giving Coniin reactions.

**Cotoin.**

A neutral body forming a yellow, crystalline mass, melting at 130°; of a not permanent acrid taste; its dust is irritating to the nostrils, producing sneezing. It chars when heated in a glass tube. Easily soluble in ether, chloroform, and alcohol; less so in carbon disulfid; not in water even 1:1000, at 100°, but if the boiling is continued for some time, it liquifies as drops, which solidify again to faint yellow particles on cooling.

(a) Ferric chlorid (Reagent 4) gives, in a boiling hot saturated watery solution, which is neutral, a voluminous brown precipitate; the fluid becomes dark red-brown first.

(b) A ten (10) per cent. lead acetate solution (*not* lead subacetate) gives a yellow turbidity in the watery Cotoin solution.

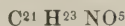
(c) Sulfuric acid changes the color of its solutions in ether or chloroform, by shaking, to a brown-yellow.

(d) Ferric chlorid solution colors the alcoholic solution red-brown.

(e) Cotoin is soluble in ammonia water and lime water (Reagents 1 and 10) with a yellow color.

(f) Strewn on sulfuric acid, it colors the latter greenish-yellow; an addition of sodium nitrite ( $\text{Na NO}^2$ ) gives a dark red color.

(g) Cotoin does not give a color reaction at first with nitric acid, but in the course of an hour, a permanently pink hue is obtained. (See Paracotoin).

**Cryptopin.**

A crystalline powder composed of six-sided prisms. Melting point 217°. Moistened with water, it gives a blue spot on red litmus paper. Soluble in acetone, benzene and chloroform; less soluble in alcohol; hardly at all in ether, carbon disulfid or water. The solutions of the salts are bitter, and produce a choking feeling in the throat.



(a) Chlorin water (Reagent 3) dissolves it with a yellow color, increasing in intensity to red on the addition of ammonia water.

(b) Sulfuric acid colors a hardly-visible particle of Cryptopin yellow at first, soon changing to red; soon pink-colored streaks flow from the fragments when strewn upon the acid, which assume a violet color, changing to blue and green:

(1) The color is blackish-blue, when a trace of ferric chlorid has been added to the acid:

(2) If a small particle of Cryptopin is triturated with a microscopical crystal of sodium nitrite ( $\text{Na NO}^2$ ) and then thrown on sulfuric acid (Reagent 21), it gives a dark violet color changing to green and, on the addition of an excess of water, to red.

(c) Cryptopin boiled with peroxid of manganese and dilute sulfuric acid of 1.110 sp. gr. gives a red filtrate.

(d) Cryptopin thrown upon Reagent 22 immediately colors the latter green.

(e) It dissolves in nitric acid with a yellow color.

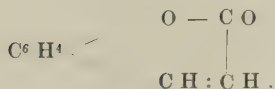
(f) Becomes yellow-colored when treated with sulfuric acid and bismuth subnitrate, as described in chapter on *Morphin*; the yellow color changes to a pure green, afterwards turning black. With molybdic acid the color changes to green, black and blue; with titanio acid, yellow, brown and pink; with tungstic acid, yellow-brown and greenish-gray.

(g) Cryptopin throws down a blue precipitate in a mixture of potassium ferricyanid and ferric chlorid solutions, after a few minutes.—See *Morphin*, “(g)”.

(h) Cryptopin decomposes  $\text{KIO}^3$  on warming with acetic acid—as described under “(h)” in chapter on *Morphin*—but *not* in the cold.

(i) Reagents 2, 6, 7, 12, 13, 14, 16, 17, 18, 19 and 24 give precipitates in a solution of Cryptopin acetate. The precipitates obtained from Reagents 2, 12, 13, 14, 17, 18 and 19 are gelatinous. Potassium iodid, sodium nitrate, and sodium thiosulfate solutions also give gelatinous precipitates in aqueous solutions of Cryptopine salts (sulfates, tartrates).

(j) Ammonia water (Reagent 1) gives an amorphous precipitate in a watery solution of Cryptopin salts, soluble in excess. Microscopical crystals soon form, however, and the alkaloid precipitates out wholly.

**Cumarin.**

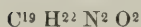
Large colorless crystals. Melting point  $67^{\circ}$ . Boiling point  $290^{\circ}$ . Sublimes unaltered. Has a sharp, bitter taste and peculiar aromatic odor, recognized by its similarity to dried *Asperula odorata*, *Anthoxanthum odoratum*, *Melilotus*, Tonka beans, etc. Does not change litmus paper. Soluble in about eight (8) parts alcohol of 0.830 sp. gr.; readily soluble in ether and chloroform; much less so in carbon disulfid; requires about six hundred (600) parts of water at  $15^{\circ}$ ; boiling water and caustic soda solution take up considerable, the latter turning yellow when boiled. Lead acetate gives a turbidity in a watery solution, saturated at  $15^{\circ}$ .

(a) Neither sulfuric or nitric acid give color reactions.

(b) If 0.010 g. Cumarin is dissolved in one (1) c. c. sulfuric acid (Reagent 21), and 0.010 g. sodium nitrate ( $\text{Na NO}^3$ ) is added to the solution, this becomes red, which color commences in the test tube from above in course of a few hours; saturated with caustic soda solution, the color changes to a pure yellow. Chloroform extracts the red color from the solution, but ether does not.

(c) White crystals are obtained if one (1) c. c. of fuming nitric acid or nitric acid (Reagent 15) mixed with three (3) drops sulfuric acid (Reagent 21), is evaporated on the water bath with 0.010 g. Cumarin. Five (5) drops or more of caustic soda solution (Reagent 20) changes this to a yellow-red fluid, which, if diluted with water to a liter, has a pure yellow color.

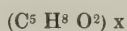
(d) A mixture of 0.020 g. Cumarin and one (1) g.  $\text{K O H}$  turns yellow when warmed in a silver dish; this color disappears on further heating; the slack colors brown afterwards. It gives the violet salicylic acid reaction with ferric chlorid solution (Reagent 4) if dissolved in a slight excess of dilute sulfuric acid 1.11 sp. gr. and one (1) drop of Reagent 4 is added to the cooled solution.

**Cuprein.\***

Small crystals, obtained by diluting the alcoholic solution with a little water. Dried at 140°, they melt at 197°. Soluble in alcohol; sparingly so in ether, benzene, chloroform or carbon disulfid—these solutions quickly turn brown.

(a) The alcoholic solution of Cuprein becomes blood-red on addition of ferric chlorid solution (Reagent 4).

(b) It gives the same green compound as quinin or quinidin, when treated with chlorin—(Reagent 3) or ammonia water (Reagent 1)—Thalleioquin reaction—Compare *Quinin*, page 107. Cuprein is related to quinin as morphin is to codein. Grimaux and Arnaud have converted Cuprein into a product, identical in all its reactions, to quinin. One molecule of an univalent acid forms basic salts with one molecule of Cuprein; usually not absolutely colorless. Watery solutions are yellow, but alcoholic solutions are not. The neutral salt, with two molecules of an univalent, or with one molecule of a bivalent acid, is yellowish, but its solutions are devoid of color.

**Digitalin. †**

An amorphous white powder of bitter taste, melting at from 210° to 217°, whereby it turns yellow. It swells up in water first, then dissolves in about 1:1000—this solution foams when shaken; it dissolves in cold alcohol of 0.931 sp. gr. 1:100, and readily in hot alcohol of 0.83 sp. gr.—If a small quantity of alcohol is used in the latter test, a kind of jelly will form on cooling, that appears amorphous under the microscope.

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\* Compare A. C. Oudemans "Contribution à la Connaissance de la Cupréin," in *Annales de l'école polytechnique de Delft, Holland*, vi., 1890, page 72.—Leiden, E. J. BRILL.

† Compare "*Digitalin verum*," by H. Kiliani in "*Arch. d. Pharmacy*," Vol. 230, 1892, page 250.

(a) Digitalin is nearly insoluble in both ether and chloroform; is thrown down as an amorphous precipitate if ether is added to an alcoholic solution, and the filtrate will yield a similar precipitate when another portion of ether is added.

(b) Dissolves with a yellow color in hydrochloric (Reagent 5) and in sulfuric (Reagent 21) acids; the solutions soon turn red.

(c) A bluish-red color reaction is obtained, if one drop of nitric acid (Reagent 15), of ferric chlorid solution (Reagent 4), or of bromin water (Reagent 2), be added to the yellow-colored sulfuric acid solution.

(d) Pure Digitalin is not affected, in one minute, by moistening with a caustic potash solution of 1.13 sp. gr.

(e) No crystals form if a small quantity Digitalin is triturated with about one hundred (100) parts of water, twenty-two (22) parts of amylic alcohol (boiling point 125° to 130°) and the whole shaken and kept for a day.

### **Diuretin.\***

A combination of Sodium theobromin and Sodium salicylate.

A somewhat crystalline powder, at first sweetish, later salty, finally of bitter taste, with an alkaline reaction to litmus as well as to phenolphthalein. It chars when heated in a glass tube, and gives off vapors of an alkaline reaction. In warm water is it soluble 1:4, but on cooling a greater part crystallizes in small microscopical crystals—not in needles.

(a) Decant one (1) c. c. of the mother liquor of these crystals, and dilute with four (4) c. c. water; neutralize with acetic acid, when a flocculent or granular precipitate of theobromin is thrown down; filter; examine under the microscope at a low power,  $\frac{50}{1}$ ; the precipitate appears in conglomerates of short prisms—not needles. This theobromin does not affect litmus and gives the same reaction with  $\text{KO}^3\text{Br}$  and acetic acid as described under “(a)”, article *Caffein*.

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\* See Pharm. Centralhalle, page 311, 29th May, 1890, “On the Assay of Diuretin and Theobromin,” by G. Vulpius, who found the Diuretin in market contained 30 to 38 per cent. theobromin; Van Itallie found a specimen with 24.5 per cent. theobromin only.

If HCl is added to the filtrate and the latter set aside, needle-like crystals of salicylic acid will form in the course of a day.

(b) To two (2) c. c. of a saturated aqueous solution of Diuretin, add one (1) drop of a tannin solution (Reagent 24). An abundant precipitate is thrown down, soluble in a Diuretin solution as well as in an excess of the Reagent. It must be observed that the dirty green color of the fluid in this reaction is due to the alkalinity of the Diuretin solution acting on the tannin.—Compare *Theobromin*, page 145.

### **Ecgonin.**



Fair sized crystals of the monoclinic system when crystallized from absolute alcohol; when water-free, melting at 198°; heated higher, they char and give off vapors of alkaline reaction, and a not disagreeable odor. Easily soluble in water; less so in chloroform; much less in ether, alcohol or carbon disulfid. A watery solution does not affect litmus paper, has a slight bitter taste, without the peculiar choking sensation produced by cocain; neither does it cause numbness.

(a) Reagents 2, 6, 7, 12, 13, 14, 16, 17 and 24 do not produce precipitates or other reactions in a watery solution, 1:100, of it.

(b) Neither nitric or sulfuric acid give any reactions. Calomel is not reduced to Hg by Ecgonin when boiled with the latter in water.

(c) Ecgonin darkens the color of a dilute (1:2) ferric chlorid solution (Reagent 4) when dissolved therein.

(d) It causes soon a green color reaction in Reagent 22.



**Emetin.**

Commercial Emetin is a yellowish-white, amorphous powder, nearly insoluble in cold water, slightly so in warm; easily soluble in ether, alcohol, chloroform and carbon disulfid. On red litmus paper, it gives an alkaline reaction if moistened with water or alcohol. The solution obtained by boiling water, is bitter when one (1) c. c. is tasted, and has an alkaline reaction only to very sensitive litmus paper.

(a) One (1) c. c. of tannin solution (Reagent 24) gives a slight turbidity in two (2) c. c. of the solution in boiling water.

(b) Twenty (20) c. c. iodine solution (Reagent 6) is required to produce a precipitate in one (1) c. c. of the aqueous Emetin solution.

(c) Precipitates are obtained when Reagents 12, 14 and 17 are added in small quantities, but only after some time with Reagent 13. Reagents 7 and 16 give voluminous precipitates; the picrate is somewhat crystalline.

(d) A faint, reddish-yellow fluid is obtained in the course of an hour by mixing one (1) c. c. of the aqueous Emetin solution with one (1) c. c. hydrochloric acid, and adding 0.005 g.  $\text{KClO}_3$  in fine crystalline powder. A variation of this test, immediately active, is had by adding to the Emetin a solution of chlorinated lime in the presence of a trace of acetic acid; this gives a bright orange to canary-yellow color reaction.

(e) The following Emetin reactions may be made with an infusion of ipecacuanha root:

(1) Agitate 0.50 g. powdered ipecac: with sixteen (16) c. c. hydrochloric acid (Reagent 5) and four (4) c. c. water; filter.

(2) To two (2) c. c. of the filtrate, add 0.010 g.  $\text{KClO}_3$ ; reaction as above.

(3) Dilute one (1) c. c. with fifty (50) c. c. water and add two (2) to three (3) c. c. of Reagent 6; the result is a clear blue fluid.—The blue color does not appear if this reaction is delayed a few hours, so that the starch has time to be converted into glucose.

(4) Reagents 12, 13, and 14 give a turbidity in the undiluted

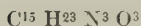
acid filtrate, but Reagents 16 and 24 cause voluminous precipitates; the precipitate from picric acid settles down very slowly, does not form crystals visibly, yet, examined under the microscope by a low power  $\frac{5}{1}^0$ , is crystalline.

(f) A neutral solution is obtained, if 0.250 g. commercial Emetin is carefully dissolved in dilute acetic acid. Reagents 11, 12, 13, 14, 16, 19 and 24 give precipitates in the neutral solution when diluted with twenty-five (25) c. c. water.

(g) Triturate 0.020 g. ammonium molybdate with five (5) drops sulfuric acid (Reagent 21): Emetin gives a brown color, soon changing to dark green, when thrown upon the foregoing and stirred with a glass rod.

The effect of Emetin on man is generally known; it exercises scarcely ever, if at all, an emetic action upon ruminants. Also it is scarcely emetic to horses. Dogs, however, are usually quite sensitive. Frogs are not sensitive.

### **Eseridin.**



Small crystals, melting at  $132^\circ$ , charring when heated higher, thereby evolving biting, stinging vapors of alkaline reaction toward litmus—the crystals do not act on litmus.

Eseridin is easily soluble in chloroform; less so in ether and alcohol; hardly in carbon disulfid. Sparingly soluble in water even at the boiling point; colors the water brownish-red at this temperature; crystals do not form on cooling; the solution is hardly bitter.

(a) Eseridin colors bromin water or chlorin water (Reagents 2 and 3) violet-red; ammonia water increases this color.

(b) Does not give a color reaction with sulfuric acid (Reagent 21)

(c) Colors nitric acid (Reagent 15) yellow first, red afterwards.  
--This solution leaves a yellowish-red residue when evaporated to

dryness, that changes slowly to green on attracting moisture from the atmosphere.

(d) Towards ammonia it acts like Eserin—see below.

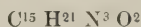
(e) Ammonia water, lime water or caustic soda solution, poured on Eseridin, becomes slowly yellow and dirty greenish; not red as with Eserin—see *Eserin* “(c)”.

(f) The differences between Eseridin and Eserin is also plainly to be seen in the reaction “(d)” described for Eserin—the former does not give a bright green color; the reaction on ammonia is the same, however, in both.

(g) A red solution is obtained by slightly warming and agitating a trace of Eseridin and the smallest particle  $\text{KIO}_3$ , with a few c. c. of water. Chloroform extracts a brown red color from this mixture; iodine is, therefore, not the cause of the darkening. If acetic acid is present, however, chloroform becomes violet from iodine—compare *Morphin* “(h)” ; the violet color, however, disappears quickly.

(h) Reagents 2, 6, 7, 12, 13, 14, 16 and 24 give precipitates in aqueous solutions of Eseridin, heavier if the solutions are previously acidulated with acetic acid. Reagents 11 and 17 do not give precipitates.

### **Eserin.**



PHYSOSTIGMIN.

Crystallizes with difficulty and softens at  $40^\circ$ . Easily soluble in ether, alcohol, chloroform, benzene, and carbon disulfide; very little in water. The watery solution is tasteless, has an alkaline reaction to litmus, and darkens to a red and dark brown fluid even in closed bottles in the dark, when occasionally exposed to light. This coloring of an aqueous solution takes place immediately when the solution is warmed. The slowly colored in the cold, or the quickly colored warm fluids, are unfit for medical or pharmaceutical purposes; alkalinity of the glass has a great deal to do with the change.

(a) An amorphous residue of a permanent blue color is obtained if a trace of the alkaloid, or of one of its salts, is evaporated in the presence of an excess of ammonia; this blue alkaloid dissolves in dilute acids with a red color: sensitiveness 0.00001 g. ( $\frac{1}{100000}$ ). The solution has a beautiful red fluorescence in reflected light; when evaporated, it leaves a residue that is green at first, changing to blue afterwards, the blue residue being soluble in water, alcohol and chloroform, but not in ether. Chloroform extracts the blue color from the watery ammoniacal solution only partially. The blue solutions are reddened at first by  $H^2S$  and discolored afterwards. The blue color is restored by expelling the  $H^2S$  on the water bath.

(b) A ten (10) per cent. solution of sodium thiosulfate discolors a spontaneously reddened aqueous solution of Eserin or its salts, immediately, when a trace of an acid is added to the mixture.  $H^2S$  has the same effect, and also hydrogen in the nascent state, developed from zinc or magnesium, when this has been added to the red Eserin solution, previously acidulated with acetic acid.

(c) When ammonia water, lime water, or caustic soda solution is poured on Eserin or one of its salts, they are colored red.—The difference with ammonia is described under “(a)”. The other alkalies do not give blue residue. (Rubroeserin solution.)

(d) A red fluid is obtained when 0.010 g. Eserin or its salicylate, 0.050 g. of slacked lime, and one (1) c. c. of water are added together. Warmed in a water bath, it turns green, and a piece of red litmus paper suspended in the test tube colors blue; a glass rod moistened with  $HCl$  gives off the well-known white clouds characteristic of an ammonia reaction.—The green solution does not lose its color by evaporation. Baryta water added to an Eserin solution gives a white precipitate, that turns red when strongly agitated; sensitive to 0.00001 g. ( $\frac{1}{100000}$ ). Dissolve for this test 0.010 g. Eserin salicylate in one hundred (100) c. c. of water (1:10,000). One (1) c. c. of this, agitated with five (5) c. c. of baryta water, gives a bright pink-red colored fluid. One (1) c. c. of the 1:10000 solution diluted to ten (10) c. c. will give a faint pink-red colored fluid, when shaken with five (5) c. c. of baryta water; one (1) c. c. = 1:100,000.

(e) Eserin thrown upon sulfuric acid (Reagent 21) or on Reagent 22, gives a yellow color reaction.

(f) Nitric acid (Reagent 15) turns it yellow first, red afterward; the residue of evaporation is yellow-red.

(g) Chlorin water (Reagent 3) gives a slight turbidity in a watery solution of Eserin salicylate 1:150. Reagents 12 and 16 give amorphous precipitates. Reagents 11, 13, 14, 17 and 24 have no appreciable effect.

(h) A very decisive identity reaction on active Eserin is had as follows: Dissolve 0.010 g. of an Eserin salt in ten (10) c. c. of water, and drop one (1) or two (2) drops of the solution in the eye; within fifteen minutes, the time varying somewhat according to individuality, the pupil becomes contracted to the size of a pin head;—this physiological experiment causes little or no inconvenience and passes off unnoticed.

(i) A reaction to determine the absence of Calabarin in Eserin (Physostigmin) is made as follows: Dissolve 0.010 g. Eserin in five (5) c. c. of three (3) per cent.  $\text{H}^2\text{SO}^4$ ; render the alkaloid free with  $\text{KCO}^3$ ; agitate with ether; decant ether, and evaporate; dissolve residue in (5) c. c. absolute alcohol, and add one (1) c. c. of a solution of potassium iodid and mercuric chlorid in absolute alcohol (in the proportions of Reagent 12). No precipitation should take place, as the mercuric iodid compound of Eserin (not of Calabarin) is soluble in alcohol.

(j) Pulverize with a coarse rasp 0.020 g. of the cotyledons of a calabar-bean, rejecting the spermodermis. Add three (3) c. c. of ammonia water (Reagent 1), and agitate frequently for two (2) hours. Filter and evaporate; the residue is of a beautiful green color and has an acid reaction when dissolved in water.—The brown hulls do not give this green residue.



**Europhen.\***

[N. B. The formula published for this substance in *Ph. Jour. & Transact.* for August, 1891, page 81, is doubtful.†]

Europhen is a light, dull yellow, amorphous powder, with a faint aromatic odor suggestive of ortho-cresol and also of saffron. It melts to a brown, transparent mass, at water-bath temperature, giving off vapors of iodine. It gives a colorless, tasteless filtrate, when boiled with water, whereby the Europhen itself conglomerates.

Easily soluble in ether, alcohol, chloroform, and fatty oils, with a yellow or reddish-yellow color; a solution in carbon disulfide is turbid and dark-colored. Water gives a bright yellow flocculent sediment in an alcoholic solution—the turbid solution does not act upon litmus paper; ferric chloride solution (Reagent 4), when evaporated with it, colors to a dirty brown.

Europhen is insoluble in water, in caustic potash or soda solutions, and in dilute acids. Concentrated sulfuric acid changes it to a dark brown powder, under liberation of iodine; water causes a white turbidity in the acid after decantation.

(a) 0.50 g. Europhen, five (5) g. zinc dust, and twenty (20) c. c. water, warmed for an hour on the water-bath, with frequent agitation, yields a colorless filtrate, from which carbon disulfide does not extract iodine; these conditions change, however, when the zinc iodide is decomposed by the addition of bromine water (Reagent 2).

(b) Water alone, when boiled with Europhen, does not show the presence of iodine when bromine water is added.

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\* Isobutylcresoliodide?

† The editor of the *Pharm. Jour. & Transactions* makes the very sensible remark that the name Europhen should be discarded, since it sounds so nearly like Euphorin (a phenylurethane compound) as to tend to considerable confusion.

**Exalgin.**

METHYLACETANILID.\*

Crystallizes in needles or prisms according to the medium used. Melting point  $102^{\circ}$ ; under water it melts at  $98^{\circ}$ . Boiling point  $245^{\circ}$ . Very soluble in chloroform, alcohol and carbon disulfid; less so in ether; soluble in cold water 1:60, in boiling water 1:2;—aqueous solutions are tasteless and neutral; Exalgin can be re-crystallized therefrom.

(a) Does not give the isonitril reaction, described under “(b)”, article *Acetanilid*, page 1, but an entirely different odor; the mixture becomes brown by adding bromin water (Reagent 2).

(b) Does not form crystals when treated as described under “(c)”, article *Acetanilid*.

(c) A red fluid is not formed, if treated as described under “(d)”, article *Acetanilid*; the color is more nearly yellow, and ammonia does not change it to a dark blue, but to a rather dirty violet.

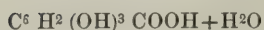
(d) Sodium nitrate or nitrite, added to a solution of Exalgin in sulfuric acid (Reagent 21), gives yellow to greenish color reactions.

(e) Exalgin at first has no effect upon Reagent 22, but later, however, changes slowly to green.

(f) Bromin water gives a strong turbidity in the solution of Exalgin in sulfuric acid (Reagent 21) when treated according to “(g)”, article *Acetanilid*; the color reaction with the acid depends somewhat on the temperature; is more yellow than brown. A few crystals are formed, not as distinctly, however, as with acetanilid. No color reaction with  $\text{Fe}^2\text{Cl}^6$ ; no precipitate with  $\text{HgCl}^2$  or tannin.

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\* It is recommended to give preference to the second name.—[J. B. N.]

**Gallic Acid.**

Melting point of the dried (100°) crystals 230°, whereby they decompose somewhat. Crystallizes in needles and prisms. Soluble in three (3) parts of boiling water, in one hundred and twenty (120) parts at 15°; in about forty (40) parts ether; in three (3) parts absolute alcohol; only slightly soluble in chloroform and in carbon disulfid. One (1) drop of a saturated aqueous solution (15°) is nearly tasteless, has an acid reaction, and decomposes sodium thiosulfate 1:50—distinction from tannin.\*

(a) Pyrogallol sublimes in crystals (compare *Pyrogallol*) when 0.050 g. Gallic acid, mixed with 0.20 g. calcium carbonate, is heated in a glass tube; the sides of the tube cover with moisture at the same time; the mixture changes to a dark-brown colored powder.

(b) Three (3) drops of a saturated aqueous solution soon crystallize when carefully brought as a top layer upon one (1) c. c. sulfuric acid (Reagent 21); these crystals dissolve colorless by shaking. No color changes occur when the acid solution is stirred with a glass rod moistened with a trace of ferric chlorid solution (Reagent 4).

(c) One (1) drop of a saturated aqueous solution (15°) gives a clear mixture with one (1) drop of copper sulfate solution (1:14) and one (1) c. c. of water; a brown precipitate forms, however, if 0.010 g. sodium acetate or calcium carbonate is shaken with the mixture.

(d) If 0.010 Gallic acid be mixed with 0.010 g. of ferrous sulfate and a few c. c. of distilled water, in a narrow test tube—the distilled water must be boiled first and allowed to cool,—even shaking of the contents does not cause any immediate coloration; later, however, the solution becomes slowly blue colored, commencing at the top, and, in the course of the day, a black flocculent precipitate settles down therein. The coloring commences very soon, if 0.001 g. sodium acetate is added, in making the reaction.

(e) 0.010 g. ammonium metavanadate ( $\text{NH}^4\text{VO}^3$ ) is soluble in four (4) c. c. of a saturated watery (15°) solution of Gallic acid, with

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\*Compare Flückiger, Pharm. Chem., I., 1888, 258.

a yellow color, soon darkening to brown; a brown precipitate forms if more ammonium vanadate is added.

(f) Gallic acid does not precipitate morphin or quinin salts from a saturated aqueous solution of the latter.

(g) It gives different color reactions with alkaline fluids. Two (2) c. c. of a watery solution will give a yellow-red mixture with one (1) c. c. ammonia water (Reagent 1). Poured on powdered calcium carbonate, it turns green. Gives a colorless mixture with an equal volume of lime water (Reagent 10), a faint green color developing a few minutes later; this takes place sooner when three (3) c. c. of lime water are taken, and the fluid in this case is darker, and changes soon to a bluish hue; a black flocculent sediment forms also.

(h) No colored mixture is obtained, however, when equal parts of Gallic acid and borax, or Gallic acid and sodium nitrate ( $\text{NaNO}_3$ ), are dissolved together in water.

(i) Gallic acid gives a precipitate in solutions of zinc sulfate only after the addition of sodium acetate.

(j) It causes a heavy precipitate in solutions of zinc acetate.

(k) With potassium dichromate it acts like tannin.

### Gelsemin.

$\text{C}^{22} \text{H}^{28} \text{N}^2 \text{O}^4$ —Gerrard.

It is a white, amorphous powder, easily soluble in alcohol, ether and chloroform. Scarcely in water, which solution has a very bitter taste. Melting point  $45^\circ$ , whereby it fuses to a colorless liquid, solidifying, on cooling, to a transparent mass. It dilates the pupil. It has strong basic properties; forms crystalline salts.\*

(a) Add to a small particle (0.002 g.) two to three (2 to 3) drops concentrated  $\text{H}^2 \text{SO}^4$  (Reagent 21); no reaction follows; it dissolves colorless. But if a few milligram peroxid of manganese are stirred in, with a glass rod, cherry-red streaks flow from the  $\text{MnO}^2$ . This reaction is said to have similarity to a strychnin reaction—N. B. If *Gelseminin* is present, olive-green colors com-

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\* Compare F. A. Thompson's "A Study of the Alkaloids of Gelsemium Root and some of their Crystallizable Salts," in *Pharm. Era*, 1887, page 3.

mence to appear in five (5) minutes on the edges of the mixture.—Writer [J. B. N.] found that no mistakes can be made between Gelsemin and strychnin, when use is made of sulfuric acid containing potassium permanganate (Reagent 23), instead of making the reaction according to the previous prescription. Sufficient Strychnin, a strychnin salt, or an aqueous solution of either, dropped into sulfuric acid containing potassium permanganate, gives an intense *blue* color reaction, besides the purple color.

Gelsemin, a Gelsemin salt, *Gelseminin*, or an aqueous solution of either, gives, 1st, *never* the blue hue, always a cherry-red; and 2nd, its color reaction fades, in less than a minute, to a colorless fluid, while the end reaction of strychnin remains longer than twenty-four hours. Proper proportions are: A few drops of a solution of 0.002 g. of a Gelsemin or of a *Gelseminin* salt, into two (2) c. c. of water, added to (3) c. c. of Reagent 23. Compare *Strychnin*, page 136.

(b) Dissolve 0.002 g. of a Gelsemin salt into one (1) drop of  $\text{H}^2\text{SO}^4$  (Reagent 21), add 0.005 g. finely pulverized sugar to this acid solution. The sugar colors red. Soon purple and bluish hues appear in the mixture, which are fairly constant, for an hour. Finally the sugar chars. This reaction fails in larger doses. *Gelseminin*, or a *Gelseminin* salt, acts the same.

(c) Drop quietly 0.005 g. of either of the two alkaloids, or of one of their salts, without trying to dissolve it, into five (5) c. c. of a very dilute (only slightly greenish-brown) mixture of a freshly prepared ten (10) per cent. solution of potassium ferricyanid and one (1) drop of Reagent 4. The alkaloids, lying at the bottom (this test is nicely to be made in a so called champagne glass), are soon covered with a precipitate of Berlin blue, which is sharply to be seen in the greenish fluid. Within an hour a precipitate of Berlin blue settles from the whole fluid.

(d) Add a few milligram of Gelsemin to three (3) drops of nitric acid (Reagent 15); no color reaction occurs. There is *Gelseminin* present if, after a little, the edges of the acid commence to color dark grass-green, and if the solution leaves a green residue when spontaneously evaporated.

(e) Add a few milligrams to a freshly prepared mixture of 0.020 g. ammonium molybdate and five (5) drops of sulfuric acid (Reagent 21).—*Gelseminin* is present if a violet color reaction



takes place; if it has been washed out (as described below) no violet color reaction takes place, only a brown.

(f) Spread five (5) drops of Reagent 22 out to a thin film, and drop a few separate particles of Gelsemin on it. A soon disappearing purple spot forms around every particle of the alkaloid.

(g) Reagents 2, 7, 12, 13, 16 and 17 give precipitates in dilute solutions of the alkaloid and its salts; so do auricchlorid five (5) per cent. and platin chlorid ten (10) per cent., solutions.

(h) Ten (10) per cent. potassa-soda and caustic ammonia solutions throw down amorphous white precipitates in weak solutions of the salts of Gelsemin that are soluble in large excess of the reagents.

(i) To verify the identity reactions of Gelsemin and occasionally on *Gelseminin*, dilute ten (10) c. c. fluid extract gelsemium sempervirens with fifteen (15) c. c. of water; add q. s. of a ten (10) per cent. lead acetate solution; filter; remove lead with sodium phosphate; filter; make carefully alkaline with  $\text{KCO}_3$ ; agitate with ether; decant ether; evaporate. Wash ethereal residue ("A") successively with twenty-five (25), ten (10), and five (5) c. c. of ice-cold water; evaporate to dryness; it is highly fluorescent (*Æsculin*—Gelsemic acid); call it residue "B".\*

Redissolve residue "B" in ether, evaporate part of the solution to dryness, and submit the residue to the reactions described above "(a)", "(b)" and "(c)".

(a) Gives no more cherry-red *streaks* after the addition of  $\text{MnO}_2$ , but an intense dark cherry-red color reaction throughout the whole

## \*GELSEMIC ACID.

Large prisms from boiling water;  
insoluble in  $\text{HCl}$ ;  
not decidedly acid;  
fluorescence rather greenish;  
composition  $\text{C}^{30} \text{H}^{34} \text{O}^{19} + 2 \text{H}_2\text{O}$ ;  
losing  $2\text{H}_2\text{O}$  only near the melting point,  $197^\circ$ .  
gives a reddish solution with  $\text{SO}^4\text{H}^2$  (concentrated);  
splits up very slowly with dilute acids at  $100^\circ$ ;  
nearly insoluble in cold  $\text{CS}_2$ , more soluble in warm  $\text{CS}_2$ ;  
soluble in 231 parts  $\text{C HCl}^3$  even at  $0^\circ$ .

## ÆSCULIN.

small crystals from water;  
readily soluble in  $\text{HCl}$ ;  
distinctly reddening litmus;  
fluorescent displaying a blue hue;  
composition  $(\text{C}^{16} \text{H}^{16} \text{O}^9)^2 + 3 \text{H}_2\text{O}$ , giving off two (2) mol. water at  $110^\circ$ , one near the melting point,  $197^\circ$   
quickly charred by  $\text{SO}^4 \text{H}^2$   
readily splitting up with dilute acids, even at  $100^\circ$ .  
Very sparingly soluble even in warm  $\text{CS}_2$   
insoluble in warm and in cold  $\text{C HCl}^3$ .

mixture; in a few minutes olive-green color shades form on the edges.

(b) A grass-green color reaction.

(c) Violet color reaction, changing to chocolate brown. Repeat the test, described before, with residue "A".

Gelseminin is a white, amorphous powder, melting at 110–112° (Spiegel).\*

Gelseminin is very bitter, amorphous, easily soluble in alcohol, ether, and chloroform; less soluble in water.

It separates out in "oily" drops, when its solution in alcohol is diluted with water; these "drops" solidify without crystallizing.

They leave a colorless, or somewhat yellow colored "sirupi" residue, when enough water has been added to dissolve them, and this solution is evaporated.

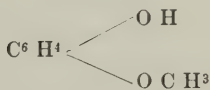
Gelseminin,  $C^{22} H^{26} N^2 O^3$  (Spiegel).

It is easy to separate Gelseminin from Gelsemin, to which F. A. Thompson claims priority, the hydrochlorid of the latter being soluble with difficulty, while the hydrochlorid of Gelseminin is easily soluble in water; insoluble in cold absolute alcohol.

The solutions of the alkaloids have a peculiar odor that has been compared to the odor of the flowers of *Robinia pseudacacia*.†

Gelseminin forms yellow salts. The nitrate is soluble in alcohol; the sulfate in water and in alcohol.

### Guaiacol.



This is a colorless, clear, neutral liquid, boiling at 200° (sp. gr. 1.17) with an odor and taste suggestive of creasote. Miscible with ether, alcohol, chloroform, caustic soda solution and carbon disulfid; slightly soluble in glycerol, water, and liquid paraffin; one

\* L. Spiegel, in "Berichte der Deutsche Chem. Gesellschaft," No. 8, May 15, 1893, page 1057—"Ueber Gelseminin."

† Proceedings of the Am. Pharm. Assoc., 1887, XXXV, 118.

(1) part Guaiacol dissolves in about two hundred (200) parts water at normal temperature.

(a) Ferric chlorid solution (Reagent 4) gives a brown turbidity in the watery solution.

(b) A pure blue colored fluid is obtained, however, by the addition of a small quantity of ferric chlorid solution (Reagent 4) to an alcoholic solution of Guaiacol; the blue color fades to green.

(c) Sulfuric acid (Reagent 21) dissolves Guaiacol with a yellow-red color, considerable heat being evolved in the process.

(d) A yellow fluid changing to a bright red is obtained by mixing one (1) drop Guaiacol, five (5) drops chloroform, and ten (10) drops sulfuric acid; the chloroform separates out colorless.

(e) One (1) drop of Guaiacol dissolves with a dark-brown color in two (2) c. c. of Reagent 22.

(f) The least trace of Guaiacol dissolves in nitric acid (Reagent 15) with a bright red color, soon changing to a dark brown-red; large quantities with a violent action.

(g) Guaiacol causes a voluminous precipitate in lead acetate solutions; not in lead subacetate.

(h) A colorless micro-crystalline combination of Guaiacol and calcium is obtained by agitating 0.10 g. slacked lime and ten (10) c. c. water, with four (4) c. c. Guaiacol (*see i*); it forms also, in course of a day, by agitating in a flask, four (4) c. c. Guaiacol with two hundred (200) c. c. of lime water. The crystalline potassium compound of Guaiacol is similarly obtained from one (1) c. c. Guaiacol and two (2) c. c. of a caustic potash solution of 1.14 sp. gr.

(i) Guaiacol changes to a green and violet colored fluid in contact with alkaline fluids and the atmosphere.

### **Guaiacol Carbonate.**



Odorless, micro-crystalline scales of a very slight aromatic taste. Melting point between 86°–90°; gives off vapors of a slight aromatic odor when heated. Soluble in ether, alcohol, chloroform and carbon disulfid, crystallizing when these solutions are evapor-

ated. Caustic alkalies do not act upon it; neither has sulfuric or nitric acid any effect, nor Reagent 4.

(a) Reagent 22 gives a red color reaction which changes to brown, and finally to green.

(b) It gives an intense and permanent red color with concentrated sulfuric acid (Reagent 21) and sodium nitrite ( $\text{NO}^2 \text{Na}$ ). A faintly yellowish or brownish hue is developed if sodium *nitrate* ( $\text{NO}^3 \text{Na}$ ) is substituted for the nitrite.

Guaiacol carbonate boiled with a large quantity of water yields, on cooling, a small quantity of crystals; the filtrate gives no evidence of the presence of Guaiacol carbonate, if treated with concentrated  $\text{H}^2\text{SO}^4$  and  $\text{NO}^2 \text{Na}$ .

## Homatropin.



HOMATROPEIN. OXYTOLUYLATROPEIN.

Has a melting point of  $98^\circ$ ; is soluble in ether, alcohol and chloroform; less soluble in water and in carbon disulfid; it crystallizes easily from the latter menstruum, but less satisfactorily from ether or chloroform.

(a) Towards litmus and phenolphthalein paper, it acts like *Atropin* (page 16).

(b) Has also similar reaction to atropin, with the tests mentioned under “(a)”, “(d)”, “(g)” and “(h)”, article *Atropin*.

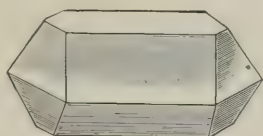
(c) Reagents 12 and 14 give precipitates in a watery solution which do not crystallize.

(d) Dissolve 0.002 g. Homatropin in one (1) drop nitric acid (Reagent 15); evaporate to dryness, and add an alcoholic KOH solution (1:5) to the residue; a distinctly yellow color is produced.—Compare *Atropin*.

(e) Dissolve 0.005 g. of one of its salts in a little water—Homatropin being very deliquescent, is usually met in pharmacy as a hydrobromid; make alkaline with ammonia; agitate in a separator with ten (10) c. c. of  $\text{CHCl}^3$ ; collect the  $\text{CHCl}^3$ ; evaporate freely.

Now make a two (2) per cent. solution of  $\text{HgCl}_2$  in fifty (50) per cent. alcohol, and add ten (10) drops thereof to the residue from the evaporation of  $\text{CHCl}_3$ ; warm slightly; a brick-red precipitate is formed.

(f) Dissolve 0.005 g. of it in ten (10) c. c. of boiling acidulated ( $\text{HCl}$ ) water; add q. s. of a five (5) per cent.  $\text{AuCl}_3$  solution and allow the fluid to cool. Crystallizes in short prisms, when seen by a low power under the microscope.

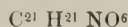


J. B. N.

HOMATROPIN GOLDCHLORID.

(g) Homatropin has mydriatic properties similar to atropin, but the effect is not so persistent or lasting.

### Hydrastin.\*



Forms short, shining, four-sided prisms when slowly crystallized from ether or chloroform, colorless or somewhat opalescent when pure. Melting point  $132^\circ$ , solidifying again to a brownish-yellow mass; it decomposes when heated higher and gives off alkaline vapors. It is affected by light, which colors it yellow. Soluble in two (2) parts of chloroform, eighty-four (84) parts of ether, one hundred and twenty (120) parts of alcohol; nearly insoluble in petroleum ether and in water. Crystals form, however, in a watery solution, saturated at the boiling point, when the liquid is allowed to cool slowly; this fluid is faintly blue fluorescent, and a drop of nitric acid (Reagent 15) increases its property, changing the tinge to a greenish hue. One (1) c. c. of the watery solution has a very faint bitter taste; no effect on litmus paper.

\* Compare Hydrastin by D. Vitali in Amer. Jour. of Pharmacy for August, '92, page 414.



(a) Reagents 2, 6, 7, 12, 16 and 24, or a lead acetate solution ten (10) per cent., gives amorphous precipitates in an aqueous hydrastin solution. Reagents 11, 13, 17 and 19 do not give precipitates.

(b) Aqueous solutions of the salts of Hydrastin (acetate especially) have an acid reaction on litmus paper, and taste very bitter, with a peculiar choking sensation. The solution of the acetate is greenish blue fluorescent, when not too dilute.

(c) Reagents 9, 13, 14, 16, 17, 18 and 24 give an amorphous precipitate in watery solutions of the salts of Hydrastin.

(d) Ammonia water and lime water set Hydrastin free from its compounds, whereby it forms crystals.

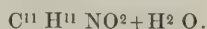
(e) *Color reactions with acids*:—Thrown on sulfuric acid (Reagent 21) it colors the latter yellow, changing to purple. Nitric acid (Reagent 15) colors slowly yellow, if present in minimal quantities; the color is orange-red if the alkaloid is present in a larger quantity; a green-blue fluorescent fluid is obtained with this acid test, by diluting with water.

(f) The smallest particle Hydrastin colors Reagent 22 bright red.

(g) A dark green color reaction is obtained from a small particle of Hydrastin, when strewn upon a mixture of 0.020 g. ammonium molybdate, and five (5) drops sulfuric acid (Reagent 21). Difference from Morphin. Red-brown color reactions, changing to yellow, are had by substituting titanate acid for molybdic acid. The tungstates produce a faint, brownish-lilac color.

(h) Yellow to brown-yellow, red-yellow and dark brown color changes are obtained, if a small quantity bismuth subnitrate is triturated to a soft mass with a few drops of sulfuric acid (Reagent 21), and a few particles Hydrastin are strewn thereon—this reaction is somewhat similar to that of morphin with bismuth sub-nitrate, with which it cannot, however, be interchanged.

### **Hydrastinin.**



Hydrastinin like homatropin, hyoscin and pilocarpin, is usually met with as a salt, not as the pure alkaloid, as the latter is too hygroscopic.

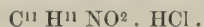
The pure alkaloid forms white crystals, with a melting point of  $116^{\circ}$ . Soluble in water, the solution being fluorescent, very bitter, and alkaline toward litmus paper; soluble in ether, alcohol, chloroform, benzene and petroleum ether.

(a) General reagents for alkaloids give precipitates in the watery solution of it.

(b) One drop sulfuric acid (Reagent 21) colors yellow on contact with a small particle of Hydrastinin.

(c) Touched with a pointed glass rod, moistened with a trace  $\text{HNO}_3$ , this color increases to a fairly permanent brown-yellow.

### **Hydrastinin Hydrochlorid.**



Is of yellowish hue; does not form distinct crystals. Melting point  $212^{\circ}$ , when it turns red or brown, giving off vapors of an acid reaction. Soluble in half its weight of water, which solution is bitter and acid to litmus.—The color is not perceptible in a 1:500 dilution. The aqueous solution becomes fluorescent on addition of  $\text{NO}^3 \text{H}$  or of lime water (Reagent 10). The salt gives a yellow solution with lime water; is also soluble in alcohol; very sparingly so in ether, chloroform, and in carbon disulfid. A 1:50 solution gives precipitates with Reagents 2, 6, 7, 12, 13, 14, 16 and 17—with the latter (17) even in a 1:500 dilution. The precipitates formed by Reagents 13, 14, 16 and 17 are crystalline. Reagents 11, 19 and 24 do not give precipitates in a 1:50 solution.

Hydrastinin hydrochlorid dissolves in nitric and sulfuric acid with a yellow color. Dissolve 0.002 g. Hydrastinin hydrochlorid in two (2) drops of nitric acid (Reagent 15); evaporate to dryness; allow to cool. Now, add to the dry-brown colored residue, a few drops of an alcoholic solution of  $\text{KOH}$  (1:5), and evaporate again. The color of the residue is greenish-brown. This greenish tinge is already noticeable when the dish, in which the acid has been evaporated, is used for the alcoholic potash while yet warm.

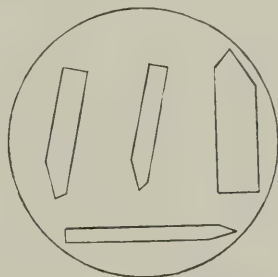
**Hyoscin.** $C^{17}H^{23}NO^3$ .

Hyoscin is, at the normal temperature, an amorphous, transparent, semi-liquid, balsam-like substance. Is usually met as a sulfate or hydrobromid. It is very poisonous, far more so than hyoscyamin.

(a) It does not throw down  $HgO$ , when a solution of a neutral salt is treated as described under "(a)", article *Atropin*.

(b) Neither does a like solution affect calomel.

(c) The hydrobromid requires four (4) parts of water of  $15^\circ$  and 21.5 parts of alcohol, of 0.82 sp. gr. for a solution.—(Merck.) The dried salt melts at  $174^\circ$  (corrected). Commercial Hyoscin hydrobromid (Trommsdorff) was found by writer [J. B. N.] to melt, water-free, at  $198^\circ$  and to give a gold chlorid dbbl. salt, in the form of long, flat, well-defined needles, when recrystallized from hot acidulated water. See figure:



*Ad Nat del JBN.*  
29

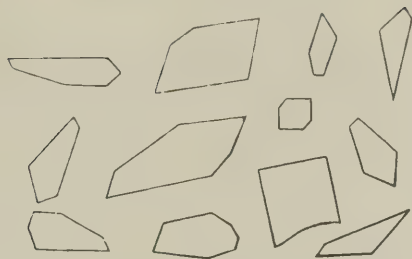
Scopolamin gold chlorid crystallizes in needles.\*

Other commercial samples of Hyoscin hydrobromid melted (dry) at  $179^\circ$ ,  $186^\circ$  [J. B. N.] the latter sample yielding a gold chlorid dbbl. salt melting at  $192^\circ$  (corr.).

(d) Prepare a gold chlorid of Hyoscin from one of its salts, as described under *Atropin* "(j)", page 17; collect, wash, dry, and take a melting point determination. The crystals melt at  $198^\circ$ .

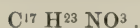
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\*Archiv der Pharmacie, 1890, page 436 and 437; Archiv der Pharmacie, 1891, page 518. Chemiker Zeitung, 1892, No. 21. E. Schmidt (Marburg) has proved that the principal base of *Scopola* root has a composition different from Hyoscin, and that it is not isomeric with atropin and hyoscyamin.



*Ad Nat del. JBN.*  
HYOSCIN GOLD CHLORID.

### Hyoscyamin.



Long, white, silky needles, in pharmacies usually found compressed into cubes. Melting point  $108.5^{\circ}$ ; liquifies under boiling water, without crystallization. Physiological effect similar to that of atropin; towards Reagents it also exhibits a close resemblance to the latter.

Hyoscyamin hydrobromate dissolves in 0.34 parts of water at  $15^{\circ}$  and in 2.2 parts of alcohol of 0.82 sp. gr. Melts at  $149-150^{\circ}$  (Merck, Ph. J. & Trans., Jan. 28, 1893.) Its aurochlorid prepared as directed for hyoscin, melts at  $160^{\circ}$ , and gives crystals\* of this form:



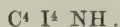
*Ad Nat del. JBN.*  
HYOSCYAMIN GOLD CHLORID.

\*N. B.—These crystal forms are only to be considered as circumstantial and additional evidence; not as positive identity reactions in the way they are here given. When all the

Rhizoma scopolia carniolica is used considerably as a source for Hyoscyamin, or unintentionally for atropin.

An aurochlorid prepared of the alkaloid from a rhizoma scopolia carniolica, Jacq.  $\alpha$ -longifolia, obtained through the courtesy of Prof. C. A. J. A. Oudemans (the living plant being verified by writer [J. B. N.] to answer to the description in De Candolle's Prodomus, Vol. 13, part 1, page 555), yielded crystals, closely resembling Hyoscyamin goldchlorid, recrystallized from hot acidulated water.

### **Iodol.**



#### **TETRAIODOPYRROL.**

A whitish or pale yellow crystalline powder, odorless when strictly pure, but usually with a faint odor. Becomes brown when heated on the water bath and loses iodine; explodes when heated to  $140^{\circ}$ , giving off violet vapors and leaving a shining charcoal. It is very little soluble in boiling water; fine needle-like crystals of Iodol form, however, when the fluid is allowed to cool. The filtrate contains 1:5000 parts. Decomposes when boiled with water.

Iodol is easily soluble in ether, alcohol and carbon disulfid; less so in chloroform. White, long, thread-like crystals form when these solutions are freely evaporated; in course of time the solutions become brown colored. Dark brown crystals, that are nearly insoluble in carbon disulfid, form, too, in time, in an alcoholic solution of Iodol.

(a) Iodol is easily soluble in ammonia water (Reagent 1) on warming; if the solution is allowed to cool, it recrystallizes. No precipitate is given in the mother liquor by  $\frac{N}{10}$  silver solution, not even when acidulated with nitric acid (Reagent 15).

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conditions under which these crystals are obtained are not absolutely equal, they may vary and are confusing instead of convincing.

Geometrical definitions lie outside the scope of this book, but they are, if correctly obtained, just as characteristic as the melting point. Very slight contaminations with Atropin lower the melting point of Hyoscyamin gold chlorid quite perceptibly.—(J. B. N.)



(b) A sediment of shining, black, heavy crystals is formed if 0.050 g. Iodol, 0.20 g. mercuric chlorid, and five (5) c. c. of water are boiled together; they are formed, also, but more slowly, when 0.050 g. Iodol is warmed for hours with five (5) c. c. of Reagents 13 or 14.

(c) 0.020 g. of it strewn upon two (2) c. c. sulfuric acid (Reagent 21), colors the latter yellow, green and brown. A brighter and more constant green color is obtained, when two (2) drops of a ferric chlorid solution (Reagent 4) is added to the acid.

(d) Boiling HCl decomposes Iodol, and the solution colors brown giving off violet vapors of iodine.

(e) Nitric acid (Reagent 15) has very little effect upon it even at water bath temperature; it decomposes it, however, boiling and induces a red color.

(f) A red fluid, changing to brown in a few minutes, is obtained, if 0.020 g. Iodol is agitated with two (2) c. c. of Reagent 22.

(g) A dark green residue, with brown edges, is obtained, if 0.005 g. Iodol is slowly evaporated in a flat bottomed dish, with two (2) c. c. of water and one (1) drop of ferric chlorid solution (Reagent 4).

(h) Addition of two (2) drops of a  $\frac{N}{16}$  silver solution to 0.020 g. Iodol, dissolved in ten (10) c. c. of alcohol of 0.83 sp. gr., in the dark, reduces silver; the fluid becomes turbid, green to violet colored, and clears up slowly.

(i)  $\frac{N}{16}$  silver solution causes a precipitate of yellow silver iodid in the fluid obtained, when 0.005 g. Iodol, 0.025 g. zinc or magnesium dust, and five (5) c. c. of water are boiled together and filtered. Metallic silver, which separates at the same time, may cover the yellow color of the iodid; often the filtrate is red or green.

**Laudanin.**

Laudanin forms small rhombic crystals, when obtained from dilute alcohol, melting point  $166^{\circ}$ . Gives a blue spot on moist, red litmus paper. Is easily soluble in chloroform; less so in strong alcohol in the cold; in ether 1:647, at  $18^{\circ}$ ; in carbon disulfid with difficulty; soluble in Na (OH).\*

(a) Colors chlorin water yellow, or faintly red, when agitated therewith, which changes to a brown hue on addition of ammonia water (Reagent 1).

(b) At first the alkaloid does not give any color reaction, when strewn upon sulfuric acid (Reagent 21); a little later, however, a pink color turning to red is developed. A dark carmin-red color reaction is obtained when a drop of ferric chlorid solution (Reagent 4—diluted 1:10) is added to the sulfuric acid (Reagent 21) by means of pointed glass rod; the red color soon darkens into red-brown.

(c) Laudanin colors black, changing to a red-brown when a very small particle of sodium nitrate ( $\text{Na NO}_3$ ) is added to the sulfuric acid (Reagent 21).

(d) It colors red-brown when strewn on nitric acid (Reagent 15).

(e) A permanent green colored fluid is obtained when a few mgr. are agitated with ten (10) c. c. of a very dilute, nearly colorless ferric chlorid solution—one (1) drop of Reagent 4 to twenty-five (25) c. c. of water. Neither chloroform or carbon disulfid takes the color out.

(f) Laudanin gives the same reaction when treated as described under *Morphin*, “(d)”, “(g)” and “(h)”, page 70.

(g) The watery solutions of its acetate are bitter.

(h) Reagents 2, 6, 7, 12, 13, 14, 16, 17, 18, 19, and 24 cause turbidity, or give amorphous precipitates in the watery solutions of its salts.

(i) Saturated solutions of potassium iodid (KI) or sodium

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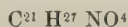
\*Pure Laudanin, contrary to Hesse's statement, is optically inactive in alcoholic as well as in acid solutions. G. Goldschmiedt in *Monatsh.* 13, 691-696, by J. o. the Chem. Soc. March 1893, page 181.

nitrate ( $\text{Na NO}_3$ ) give also precipitates in watery solution of Laudanin acetate.

(j) Ammonia water (Reagent 1) gives a precipitate in a Laudanin acetate solution, which is partially soluble in excess of the reagent; after a while, however, Laudanin forms crystals again.

Laudanin can be recrystallized from boiling water when the latter is allowed to cool.

### Laudanosin.



Crystallizes in long needles from carbon disulfid. Is soluble in ether, alcohol and chloroform; insoluble in water. Melting point  $89^\circ$ . Solidifies clear, colorless, amorphous, but soon recrystallizes when warmed to about  $70^\circ$ . Gives blue spots when strewn upon moist red litmus paper.

(a) Laudanosin colors chlorin water (Reagent 3) yellow; ammonia water develops from the yellow a red.

(b) Dissolves in sulfuric acid (Reagent 21) with a lilac color soon fading. It is enough to touch the drop of sulfuric acid very slightly at the top, with a glass rod of the size of a match moistened with a trace of ferric chlorid (Reagent 4) to change this color to an intense violet.

(c) A bright red is obtained when a mixture of 0.005 g. Laudanosin and 0.005 g. sodium nitrite ( $\text{Na NO}_2$ ) is strewn upon a few drops of sulfuric acid (Reagent 21).

(d) A faintly pink color reaction is obtained when cane sugar is substituted for sodium nitrite ( $\text{Na NO}_2$ ); the color changes to brown yellow. See *Morphin*, "(f)", page 76.

(e) A yellow color reaction is obtained with nitric acid (Reagent 15).

(f) Laudanosin gives in the bismuth subnitrate reaction (as described under "(d)", article *Morphin*, page 76), a brownish-black color reaction, changing to brownish-red; ammonium molybdate gives a purple color, changing to blue; titanin acid a lilac color,

turning brown. The tungstates have little or no action upon Laudanosin.

(g) Laudanosin does not give the Berlin-blue color reaction with the mixture of ferric chlorid and potassium ferricyanid immediately as morphin does; but in course of a few hours, it acts similarly to the latter.

(h) Laudanosin gives a red solution with potassium iodate ( $\text{KIO}_3$ ). No iodine is separated.—See article Morphin, “(h)”, page 77.

(i) Reagents 6, 12, 13, 14, 16 and 24 give precipitates in the watery solution of Laudanosin acetate; Reagents 17 and 19 do not.—These watery solutions taste bitter.

### **Menthol.**



Menthol forms long crystals of a somewhat indefinite shape (usually met as colorless needles) with a peppermint odor, subliming spontaneously when kept in stock, and evaporating quickly on the water bath. Melting point  $43^\circ$ . Boiling at  $212^\circ$ . Dissolves easily in ether, alcohol, chloroform, liquid paraffin, glacial acetic acid and carbon disulfid; insoluble in water and in caustic potash and soda solutions. Applied to the skin, it causes a peculiar sensation of cold.

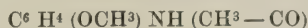
(a) It liquefies when two (2) drops of acetic acid of 1.068 sp. gr. are added to 0.10 g. Menthol; the liquid becomes turbid on the addition of 0.5 c. c. acid and when left to itself separates into two clear layers. 0.10 g. Menthol is clearly soluble in three (3) c. c. acetic acid; Menthol separates out in the form of drops, when four (4) c. c. water are added to this solution.

(b) A yellow liquid changing to a brown-red turbid one is obtained by shaking 0.50 g. Menthol with twenty (20) c. c. sulfuric acid (Reagent 21); a clear, colorless top layer, of about one-half (0.5) c. c., separates from this, in the course of a day, consisting of *Methen*,  $\text{C}^{10} \text{H}^{18}$ , which does *not* have the odor of Menthol.

(c) Nitric acid has hardly any action on Menthol.

(d) Menthol liquefies when mixed with chloral hydrate, phenol resorcinol or thymol, in the proportion of two (2) parts of the former to one (1) of the latter.

### Methacetin.



PARAOXYMETHYLACETANILID.

Colorless and odorless scaly crystals or needles, with a taste suggestive of acetanilid. Melting point  $127^{\circ}$ ; at higher temperatures sublimes unaltered. Easily soluble in acetone, alcohol and chloroform; less soluble in ether and carbon disulfid—in ether, free from alcohol, 0.6 part dissolves in one hundred (0.6:100) at  $15^{\circ}$ , 0.7 part (0.7:100) at  $20^{\circ}$ ; soluble in boiling water 1:12; of  $15^{\circ}$ , 1:500—Compare *Phenacetin*, page 91; soluble in glycerol of 1.25 sp. gr., 1:100 at  $70^{\circ}$ ; and in olive oil 1:100 at  $90^{\circ}$ .

(a) The excess of crystals melt if a part Methacetin is boiled with a quantity water insufficient for its solution—Compare similar test on *Phenacetin*, page 91.

(b) Methacetin does not affect litmus.

(c) Methacetin is easily soluble in sulfuric acid (Reagent 21), the solution being colorless at water-bath temperature, but of violet hue when heated higher. Crystals form, when a solution of 0.10 g Methacetin in two (2) c. c. warm sulfuric acid, is (carefully!) diluted with two (2) c. c. of water and the dilution allowed to cool.

(d) Reagent 22 becomes colorless, when Methacetin is strewn upon it.

(e) 0.10 g. Methacetin dissolves easily in five (5) c. c. hydrochloric acid (Reagent 5).—Compare the same test on *Phenacetin*, page 91; this solution is colorless, and crystals of Methacetin form in a few hours; they do not form when a stronger acid is taken, at least not until after a much longer time.

(f) A red color is obtained when 0.010 g. Methacetin is heated to boiling with one-half (0.5) c. c. hydrochloric acid, cooled, diluted with three (3) c. c. water, and one (1) drop of Reagent 17 added.



(g) If 0.10 g. Methacetin is warmed with one (1) c. c. caustic soda solution (Reagent 20), and three (3) drops chloroform, it gives off the offensive poisonous odor of phenylisocyanid (the isonitril reaction).

(h) A bright green colored fluid is obtained when a mixture of 0.030 g. Methacetin and 0.030 g. sodium nitrate ( $\text{Na NO}_3$ ) is strewn upon one (1) c. c. sulfuric acid (Reagent 21). The acid is violet colored when sodium nitrite ( $\text{Na NO}_2$ ) has been taken instead of the nitrate.

(i) Methacetin (0.20 g.) is clearly soluble in two (2) c. c. nitric acid (Reagent 15) with a red-yellow color; this solution soon becomes turbid, heated, and solidifies to a crystalline mass.—Compare *Phenacetin*, page 92. A yellow-red fluid is obtained when this is dissolved in fifteen (15) c. c. of water at the boiling point; short, yellow-red prisms form, when this fluid is allowed to cool, that differ in shape from the crystals obtained in a similar reaction with *Phenacetin*—Compare “(j)”, page 92.

(j) A filtrate in which salicylic acid can be detected by its color reaction with ferric chlorid solution (Reagent 4), is obtained when 0.010 g. Methacetin, mixed with two (2) g. zinc dust is slowly heated in a glass tube and the residue shaken with three (3) c. c. of warm water and finally filtered.

(k) 0.010 g. Methacetin, when shaken with ten (10) c. c. chlorin water (Reagent 3) colors the latter faintly red-yellow; a few drops ammonia water (Reagent 1) changes this immediately to a brown-red.—Phenacetin gives the same brown color reaction with ammonia water, but less intense than Methacetin, because the former is less soluble in chlorin water.

### **Morphin.**



The crystals of Morphin, colorless, transparent prisms when formed in a semi-watery solution, melt at  $200^\circ$ , forming a purple fluid, changing to a dark brown, later on to black. Soluble in water at  $100^\circ$ , 1:500; at  $15^\circ$  1:5000; the 1:5000 solution has an alkaline reaction to litmus, and a faintly, soon passing off, not dis-

agreeable bitter taste. One drop of ferric chlorid solution (Reagent 4) added to ten (10) c. c. of cold, saturated, watery solution of Morphin, gives a dirty greenish color, changing to violet-blue in the course of half a day. Morphin is more soluble in methyl alcohol, ethyl alcohol, amyl alcohol, acetone, and ethyl acetate than in water. A saturated alcoholic solution (33 per cent. alcohol) is also hardly bitter to writer [J. B. N.]. Almost insoluble in absolute ether or absolute chloroform—free from alcohol—in benzene and in carbon disulfid, in the crystalline state. It dissolves sparingly in ether and in chloroform, when freshly precipitated and amorphous. It dissolves to some extent in caustic potash and soda solutions, in ammonia water (Reagent 1), in baryta water and in lime water, and such are not solutions merely, since unstable morphinates are formed, which color darker and darker, when exposed to the influence of the atmosphere and light for a few weeks, being thereby decomposed.

(a) A blue fluid that can be diluted with water without fading, is obtained when a few crystals of Morphin are moistened with water, and one (1) drop of Reagent 4 is added; the alkaloid thereby becomes covered with ferric hydroxid, and a part of the ferric is reduced to a *ferrous* compound.

(b) Morphin gives no reaction with strictly pure sulfuric acid (Reagent 21) when strewn upon it in finely pulverized form, though in course of time the acid turns somewhat green; this mixture becomes dark purple or brown, when touched with a pointed glass rod moistened with a faint trace of nitric acid (Reagent 15); more nitric acid changes the color to red.

(c) Crystals of Morphin become bright red colored when strewn upon nitric acid (Reagent 15) while the acid itself becomes yellow-red: this color test of the acid is better observed when it has been previously diluted with twice its volume of water.

(d) Triturate 0.020 g. ammonium molybdate with five (5) drops sulfuric acid (Reagent 21), spread this out to a thin film, and add a trace of Morphin, when the paste becomes permanently blue colored; sensitive with certainty to 0.00001 g. Dissolve 0.010 g. Morphin in one hundred (100) c. c. water; this is 1:10,000 ("A"); dilute ten (10) c. c. of this solution to one (1) liter, and evaporate from this ten (10) c. c. to dryness, submitting the not visible residue to the freshly prepared reagent. A lilac-color appears immediately on

contact, soon changing to a permanent dark blue. A control experiment may be carried out side by side with this reaction, if 0.020 g. molybdate of ammonia is mixed with five (5) drops  $H^2SO^4$  on a watch crystal, and only a part of the sulfomolybdate used for the reaction. Pink-violet and brown-red colors are obtained when titan-ic acid is substituted for the molybdate. The reaction with a solution of titan-ic acid (0.020 g.) in sulfuric acid (Reagent 21) five (5) drops is also sensitive to a 0.00001 g. ( $\frac{1}{100,000}$  Mo). It is advisable, however, to submit 0.0001 g. ( $\frac{1}{10,000}$  g.) to the test (the residue of the evaporation of one (1) c. c. of solution "A") as the brown-red color reaction is not as distinctively bright as the blue is. A tungstate produces results similar to those obtained from titan-ic acid. Morphin gives a black, or dark brown color reaction, if bis-muth subnitrate is used; but care has to be taken that the bismuth salt is good and not too acid, else the reaction fails and a red, instead of a black color is obtained.—Compare *Codein*, *Cryptopin*, *Narcein*, *Narcotin* and *Piperin*.

(e) Morphin dissolves in Reagent 22 with a faint green color, increasing in intensity when more potassium dichromate is added. The mixture becomes at last brown colored, but in course of time the green hue may come back.

(f) A rose-red mixture is obtained by triturating together 0.020 g. Morphin with 0.010 g. cane sugar and two (2) drops sulfuric acid (Reagent 21). N. B.—Codein gives the same reaction.

(g) Morphin, as has been stated, possesses strong reducing properties; it causes a blue precipitate in a mixture of ferric chlorid and potassium ferricyanid; 0.075 g. of potassium ferricyanid is dissolved in two hundred (200) c. c. of water, to which is added one (1) c. c. of Reagent 4; a few particles of Morphin, or one of its salts, moistened with the mixture, give the foregoing reaction; the best way to observe it, is to strew the Morphin (or its salt) previously reduced to a fine powder, upon ten (10) c. c. of the ferric chlorid-potassium ferricyanid mixture in a test tube. This particular reaction for Morphin is, however, only of value in connection with other identity reactions, as many other substances have, more or less, the same reducing properties, especially in direct sunlight —*e. g.*, cork, paper, starch, sugar, hydrogen sulfid ( $H^2S$ ). The ferric chlorid—ferricyanid potassium mixture must be made

fresh on every occasion, as it cannot be preserved without decomposition.

(h) A mixture of 0.10 g.  $\text{KIO}^3$ , five (5) drops acetic acid, and five (5) c. c. water, may be warmed together on a water bath, in a scrupulously clean test tube, without decomposition; but iodine is liberated immediately upon the addition of 0.001 g. of Morphin or one of its salts; chloroform extracts it with the well-known purple color; but this, again, is not an identity reaction for Morphin alone, as codein, cryptopin, eseridin, laudanin and narcotin have the same property. *Selmi* obtained it with a ptomain.\*

(i) Bromine is not as easily liberated from  $\text{KBr O}^3$  by Morphin as is iodine from  $\text{KIO}^3$ .  $\text{KClO}^3$  is not affected by Morphin.

(j) 0.050 g. finely pulverized Morphin crystals dissolve easily in fifty (50) c. c. of lime water.—See above. Chlorine water colors this solution bright red.

(k) Strong chlorine water is colored pale yellow when agitated with Morphin or its salts. A brown to red color is obtained, at the place of contact, when this mixture is carefully overlaid with ammonia water (Reagent 1). The fluid becomes dark brown, when the reagents mix.—Compare *Methacetin*, *Phenacetin*, *Quinin-sulfate*.

(l) When 0.010 g. Morphin is evaporated on a sand bath with ten (10) c. c. of ten (10) per cent.  $\text{H}^2\text{SO}^4$ , the solution dries at the edges with a gray, somewhat purplish tinged color; the fluid itself colors brown-red.—Compare *Codein* and *Narcein*.

(m) A bright blue colored fluid is obtained, in the course of an hour, when 0.020 g. Morphin, 0.020 g. sodium nitrite ( $\text{Na NO}^2$ ) and 0.040 g. mercuric chlorid are warmed and frequently stirred on the water bath, with six (6) c. c. of water. Afterwards, the fluid becomes turbid, and a dark blue crystalline precipitate settles down that, in the course of a day, turns brown; alcohol does not destroy the blue color. This reaction may be hastened by warming the mixture over an open flame instead of on the water bath, but the color is less bright; it varies, moreover, as do many others, according to proportions. A violet blue is obtained when 0.020 g. mercuric chlorid (instead of 0.040 g.) and four (4) c. c. instead of six (6) c. c. of water are taken; with Morphin

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\* Compare *Otto*, Ausr. d. Gifte. Braunschweig, Verlag von Vieweg & S., 1884, page 101, and *Vaughan*, Ptomaines and Leucomaines, page 115. Philadelphia: Lea Bros. & Co.



salts the reaction does not succeed as well as with the alkaloid. No coloring takes place when mercuric cyanid is substituted for the chlorid; an amethyst color is obtained by employing mercuric bromid. Codein, narcein, narcotin and papaverin do not give these color reactions.

A short qualitative assay process on Morphin in tinctures or fluid extracts is made by evaporating five (5) c. c. of the given fluid to dryness, with one (1) g. of calcined magnesia. Pulverize the residue and boil with (10) c. c. acetone; filter; add a few c. c. of water and a few drops of acetic acid to the filtrate; evaporate to a minimum, and filter again; divide the filtrate equally over as many porcelain lids as are necessary for the intended Morphin reactions, and evaporate each quantity to dryness.

### **Morphin Hydrochlorid.**



Gives neutral solution with twenty-five (25) parts of water at 15°, or with one (1) part at 100°; also with fifty (50) parts of alcohol; these solutions are distinctly bitter in 1:200,000 dilution to writer [J. B. N.].

(a) A blue color reaction is obtained, when to 0.020 g. of the salt, triturated with a drop of water, one-half (0.5) c. c. of a dilute ferric chlorid solution (Reagent 4), 1 to 10, is added.

(b) It gives the characteristic reactions described under article Morphin “(b)”, “(c)”, “(d)”, “(e)”, “(f)”, “(g)” and “(h)”.

(c) Morphin tannate is so easily soluble in water, that even a saturated solution of Morphin hydrochlorid (15°) remains unchanged when tannin is added. The tannate is precipitated, however, if a piece of chalk is introduced in a mixture of two (2) c. c. of a saturated solution of the salt and one (1) c. c. of tannin solution.

(d) It is the best way to apply the reaction described for Morphin, under “(g)”, page 76, as follows:

Dissolve 0.001 g. Morphin hydrochlorid and 0.001 g. potassium



ferricyanid in five (5) c. c. of water, and add one (1) drop of Reagent 4, diluted 1:10.

(e) Crystals of Morphin soon form when four (4) c. c. of lime water (Reagent 10) are added to one (1) c. c. of a saturated aqueous Morphin hydrochlorid solution; they dissolve in an additional one (1) c. c. of lime water. The fluid colors red-yellow, when one (1) c. c. of chlorin water (Reagent 3) is added.

(f) Two (2) c. c. chlorin water (Reagent 3) cause a yellow coloring in one (1) c. c. of a saturated aqueous Morphin hydrochlorid solution, which changes to brown, on the addition of one (1) c. c. ammonia water (Reagent 1).—Compare *Quinin Hydrochlorid*, page 109.

## Naphthalene.



Large, colorless (white), thin, rhombic plates of a penetrating, disagreeable odor, with a melting point of  $80^{\circ}$ ; boiling point  $218^{\circ}$ ; sp. gr. 1.158. Sublimes easily on the water bath, and spontaneously in the summer at temperatures above  $20^{\circ}$ . Insoluble in cold water; easily in ether, alcohol, chloroform, benzene, liquid paraffin, warm acetic acid, and carbon disulfid.

(a) In the cold, concentrated sulfuric acid (Reagent 21) colors it little, if strictly pure, but if warmed on the water bath, gives a brown or red color reaction; yellow if nitric acid is substituted. The mixture becomes brown if the sulfuric acid contains a trace of nitric acid; the same color also developing slower when a trace of sodium nitrate ( $\text{NaNO}_3$ ) has been added to the sulfuric acid.

(b) A red, purple-tinged fluid is obtained when 0.10 g. Naphthalene is triturated with a pointed glass rod previously moistened with a trace of ferric chlorid solution (Reagent 4), and drop by drop ten (10) c. c. of sulfuric acid is added; the color changes to dark violet when warmed on the water bath, and becomes red, when diluted with water. Neither chloroform or carbon disulfid extract the color from this mixture.

(c) Every particle of Naphthalene turns immediately black when

strewn upon a mixture of 0.030 g. sodium nitrite ( $\text{Na NO}^2$ ) and five (5) c. c. sulfuric acid; 0.010 g. Naphthalene is enough to color the whole mixture brown-black.

(d) Two (2) c. c. sulfuric acid colors a bright red when slightly warmed and agitated with a solution of 0.050 g. Naphthalene in one (1) c. c. of chloroform; the chloroform remains colorless.

(e) Abundant yellow crystalline needles of Naphthalene picrate form if 0.090 g. Naphthalene and 0.160 g. picric acid are dissolved in four (4) c. c. of warm alcohol of 0.83 sp. gr. and the solution allowed to cool; these crystals are only slightly soluble in nitric or sulfuric acid, even on warming.

## **Naphthol.**



### ALPHA AND BETA-NAPHTHOL.

I. (a) Alpha-Naphthol crystallizes (from boiling water) in long, soft, colorless needles, soon coloring brown-red. Has a melting point of  $94^\circ$ . Is easily soluble in alcohol, ether and benzene; very little so in cold water. Can be distilled at  $278^\circ$ – $280^\circ$  with very little decomposition.

II. (b) Beta-Naphthol appears as colorless laminæ of faint aromatic odor and burning taste. Melting point  $123^\circ$ . Boiling point  $286^\circ$ , at which it sublimes unaltered. It evaporates slowly with watery vapor, when heated in an open dish on the water bath. Easily soluble in ether, alcohol, benzene, and chloroform; less so in carbon disulfid; in liquid paraffin with difficulty; in boiling water 1:76; crystallizes by cooling; in water at  $15^\circ$  1:1000.

The characteristic reactions for Alpha-Naphthol are:

(a) Shake a few lumps with fifty c. c. milk of lime; filter; add to the clear filtrate bromin water (Reagent 2). A flocculent sediment of a lilac color, soon changing to violet, is produced.

(b) Mix 0.025 g. Alpha-Naphthol with two and a half (2.5) c. c. of alcohol 94 per cent, seven and a half (7.5) c. c. water, and ten (10) drops ferric chlorid solution (Reagent 4). A yellow-red flocc-

culent sediment, soon changing to brown and afterwards to a lilac, forms in the mixture.

(c) 0.20 g. Alpha-Naphthol, 0.20 g. of mercuric chlorid, 0.10 of sodium nitrate ( $\text{Na NO}_3$ ) warmed on a water bath with ten (10) c. c. of water, give a bright red precipitate.

The characteristic reactions for Beta-Naphthol are: It is easily soluble in watery solutions of the alkalies.

(a) It colors cold sulfuric acid red-yellow; nitric acid red, whereby the crystals of  $\beta$ -Naphthol blacken. Every particle of  $\beta$ -Naphthol, that comes in contact with sulfuric acid containing a trace of nitric acid, blackens immediately.

(b) Boil one (1) g.  $\beta$ -Naphthol with one hundred (100) c. c. of water, cool to  $15^\circ$ ; filter. This filtrate colors green, when a few drops of ferric chlorid solution (Reagent 4) is added to it. It soon becomes turbid, and beautiful, white, crystal conglomerates of  $\beta$ -dinaphthol form in it, in a few hours.—Isodinaphthol,  $\text{C}^{20}\text{H}^{12}(\text{OH})^2$ . The ferric salt is hereby reduced to a ferrous compound. These crystals appear in a short time, if 0.025 g. of  $\beta$ -Naphthol is dissolved in two and a half (2.5) c. c. of alcohol of 0.83 sp. gr., seventy-five (75) c. c. of water and ten (10) drops of the ferric chlorid solution are added; the clear fluid has a yellow-green color.

(c) Shake fifty (50) c. c. milk of lime with a few crystals  $\beta$ -Naphthol, and filter, whereby a highly fluorescent solution is obtained, in which crystals of  $\beta$ -Naphthol form in large quantities after the addition of acetic or other acids. Bromin water (Reagent 2) gives a dense turbidity, turning dirty green after the addition of ammonia (Reagent 1); a dark brown flocculent sediment soon forms.

(d) Ammonia water (Reagent 1) agitated with  $\beta$ -Naphthol becomes fluorescent.

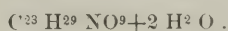
(e) 0.10 g.  $\beta$ -Naphthol and 0.160 g. of picric acid dissolve, when slightly warmed with one (1) c. c. of alcohol of 94 per cent. and one and a half (1.5) c. c. of water; on cooling, they are deposited, separately, as yellow-red crystals.

(f)  $\beta$ -Naphthol is soluble in warm concentrated sulfuric acid with a green-violet color. It becomes red, soon changing to brown-black, if it is strewn upon five (5) c. c. of sulfuric acid containing 0.030 g. of sodium nitrite ( $\text{Na NO}^2$ ).

(g) A reaction for both  $\alpha$ - and  $\beta$ -Naphthol is to dissolve 0.010

g. of the compound in five (5) drops of chloroform; add five (5) drops of a ten (10) per cent. caustic soda or potash solution; heat to 50°. The top layer turns blue. This blue layer sinks, when ether is added. The whole fluid is blue, if alcohol is added. It fades by addition of acetic acid.

### Narcein.



Needles or prisms, according to the circumstances under which it has been crystallized. Melting point near to 160°, whereby it decomposes. Soluble in alcohol; slightly in carbon disulfid and chloroform; hardly in benzene and in ether. Soluble in water at 100°, 1:100; at 15°, 1:425. Easily soluble in lime water; the solution becoming yellowish-colored and changing to red, after the addition of ehlorin water (Reagent 3). No reaction on moist litmus paper.

(a) It does not give the reaction with ferric chlorid as morphin does, described under “(a)”, page 75; neither does it give the blue precipitate in the potassium ferricyanid mixture, as morphin does.

(b) It colors sulfuric acid (Reagent 21) brownish-yellow; red, and red-brown, afterwards, when strewn upon it. The mixture becomes brown-violet, when stirred with a glass rod of the size of a match, moistened with a trace of nitric acid. A permanent cherry-red colored fluid is obtained when a solution of Narcein in diluted sulfuric acid (1.11 sp. gr.) is concentrated upon the water bath.

(c) It colors nitric acid (Reagent 15) red, which color soon fades to yellow; dilute nitric acid has no—or very little—effect upon it.—Compare *Morphin*, “(c)”, page 75.

(d) It can be evaporated down with hydrochloric acid, without showing any color reaction.

(e) Narcein gives a brownish green, changing to blue, color reaction, if treated with molybdate of ammonia and sulfuric acid, as described for *Morphin* under “(d)”, page 75; with titanilic acid, a violet to yellow-brown color, changing to a bright chocolate-brown; tungstates act less energetically. To bismuth sub-nitrate

it gives a similar reaction as morphin; the black color soon changing, however, to a lilac.

(f) Narcein does not liberate iodine from  $\text{KIO}^3$  as morphin does; iodine is, however, separated if the mixture is kept for days at the temperature of the water bath.

(g) Narcein gives a yellow-green mixture if triturated with sugar and sulfuric acid, as described under "(f)", article *Morphin*, page 76.

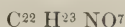
(h) A saturated watery solution ( $15^\circ$ ) of Narcein shows the following properties: Microscopically fine needles, suggestive of a tuft of hair, of a blue, green or gray color, form wherever a particle of iodine is strewn into the solution; these crystals are gray and shining, when dry. Narcein salts give the same reaction as the alkaloid; with  $\text{KIO}^3$ , as well as with iodine.

(i) Bromine water (Reagent 2) gives an amorphous precipitate of a bright yellow color in the watery Narcein solution.

(j) Narcein dissolves into chlorine water (Reagent 3), colorless; this solution becomes red colored, when ammonia water (Reagent 1) is added to it.

(k) Reagents 11, 12, 13, 14 and 19 give no precipitates in the watery Narcein solution. Reagent 17 forms a crystalline precipitate in the course of a day; Reagents 16 and 24 give voluminous, amorphous precipitates.

## Narcotin.



(ISOMER WITH GNOSCOPIN. \*)

Colorless, transparent needles. Soluble in ether, alcohol, benzene, chloroform and carbon disulfide; not in water. Melting at  $176^\circ$  to a yellow fluid, which becomes more red colored when heated higher. It has no effect on red litmus paper, when strewn upon it and moistened afterwards with alcohol or water.

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\* Gnoscopin is described in "La Constitution Chimique des Alcaloïdes Végétaux par Amé Pictet," page 211.—Paris, Masson, 1888.



(a) Narcotin does not act upon ferric chlorid solution when moistened with it.

(b) Strewn upon sulfuric acid (Reagent 21) it colors this yellow; this color changes to brown after many months. This red color appears immediately, when the acid is slightly warmed, and also if stirred with a pointed glass rod, moistened with a trace of nitric acid (Reagent 15). A solution of Narcotin in diluted sulfuric acid (1.11 sp. gr.) colors brown-red or lilac, if evaporated on the water bath.

(c) Narcotin dissolves in nitric acid (Reagent 15) with a yellow color; this color changes to red in course of an hour.

(d) A mixture of 0.020 g. of Narcotin, 0.010 g. of sugar, and two (2) drops of sulfuric acid, triturated together, colors faintly red; this color disappears soon.

(e) Narcotin colors red, if treated with bismuth subnitrate, as described under *Morphin*, page 76; green, with the mixture of ammonium molybdate and sulfuric acid; the blue color it takes afterwards is not characteristic. With titanid acid a not very constant brown color; the mixture is yellow with tungstates, brown afterwards. If the sulfuric acid has attracted too much moisture, these reactions may fail; but it is in such cases sufficient to warm the mixture slightly, to obtain the color reactions.

(f) Narcotin has no such reducing action on a mixture of ferric chlorid and potassium ferricyanid, as *Morphin* has.—See *Morphin*, page 76. Neither does it liberate, under the same conditions as morphin, iodine from  $KIO_3$ . Iodine is, however, liberated by narcein in the course of a day, or by warming the mixture for about an hour on the water bath.

(g) Ferric chlorid solution, added to a solution of narcein in sulfuric acid (Reagent 21) shortens the time that this becomes red, or increases the color caused by Narcein.

(h) Narcotin is only very slightly soluble in water. A solution made of it with boiling water, and subsequently cooled to  $15^\circ$ , is tasteless. Iodine water (Reagent 6) produces only a faint turbidity in it. Reagents 7 and 12 give heavier precipitates. Reagents 2, 13, 14, 16 and 17 do not precipitate it at all.

**Nicotin.**

A colorless, oily fluid of 1.014 sp. gr. at 15°. Boiling point 247°. Miscible with water, alcohol and ether in all proportions. Equal volumes of carbon disulfid and Nicotin give a clear solution, which becomes turbid if more carbon disulfid is added. Nicotin has a peculiar odor, suggestive of tobacco.

(a) A drop of Nicotin, introduced on a glass rod in the flame of a Bunsen burner, burns with light and sets off soot.

(b) Fifteen drops of Nicotin give with thirty (30) c. c. of water a clear solution, which has a strong alkaline reaction to litmus and phenolphthalein paper; decomposing also Calomel. This solution remains clear when warmed, which a *Coniin* solution does not.

(c) A glass rod, moistened with hydrochloric acid, gives off white clouds, when brought near Nicotin or near a watery solution of it.

(d) The watery Nicotin solution gives a precipitate in solutions of alum salts, iron chlorid and copper sulfate.—Compare “(d)”, *Coniin*, page 41. The filtrate from the copper salt is colorless.

Nicotin does not form crystals, if treated as described for *Coniin* under “(b)”, page 41; neither do they form in the reaction described under “(i)”, page 42; nor is a thiosulfate or a sulfid formed, when Nicotin acts upon  $\text{CS}_2$ ; neither is heat developed from the mutual action of sulfur and Nicotin.—Compare “(g)”, *Coniin*, page 42.

(e) Chlorin water (Reagent 3) does not give a turbidity, in a watery solution (1:50) of Nicotin; neither do Reagents 17 and 19.

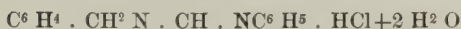
(f) Bromin water (Reagent 2) and iodin water (Reagent 6) cause considerable turbidity in the watery solution of Nicotin, which soon disappears; it reappears when a large excess of the same reagents is added. Reagent 7 gives a heavy precipitate.

Reagent 11 has no effect on a watery Nicotin solution—difference from *Coniin*.

(g) Reagent 12 gives a crystalline precipitate, forming more or less in microscopical conglomerates; Reagent 14 forms short prismatic crystals; Reagent 13, large crystals, shaped like a saw, re-

sembling crystals of salmiak; Reagent 16 forms crystalline tufts; Reagent 24 gives an amorphous precipitate—all in the watery solutions of Nicotin.

### **Orexin Hydrochlorid.\***



PHENYLDIHYDROQUINAZOLIN HYDROCHLORID.

<sup>1</sup> A white crystalline powder of permanent bitter and burning taste, melting on the water bath (80°) to brown laminæ, a slack-like mass; charring when heated higher. It violently irritates nasal mucus membrane, and induces sneezing. Soluble in water at 15°, 1:15, much less in hot water—the watery solutions have an acid reaction to litmus paper; is easily soluble in alcohol; less so in chloroform; nearly insoluble in ether and carbon disulfid.

(a) Ammonia water (Reagent 1), lime water (Reagent 10), and ten (10) per cent. caustic potash and soda solutions, give precipitates in the watery solution of Orexin hydrochlorid.

(b) Reagents 2, 6, 7, 11, 12, 13, 14, 16, 17, 18, 19 and 24 give precipitates in the watery solution.

(c) Concentrated solutions of ferric chlorid, potassium iodid, sodium acetate, sodium chlorid, and sodium thiosulfate, give also precipitates of Orexin in a concentrated watery Orexin hydrochlorid solution. These precipitates go into solution when agitated with ether, or chloroform. Silver nitrate also gives a precipitate, but silver chlorid precipitates too.

(d) The salt is colorlessly soluble in Reagents 5, 15, 21 and 22. It colors brown if warmed with Reagent 21.

(e) A brown color reaction, fading to green, takes place when a mixture of 0.020 g. Orexin hydrochlorid and 0.020 g. sodium nitrite ( $\text{Na NO}^2$ ) is strewn upon one (1) c. c. sulfuric acid (Reagent 21); the color is faintly red-yellow, when sodium *nitrate* ( $\text{Na NO}^3$ ) is substituted for nitrite.

(f) A strong carbylamin odor is developed, when equal parts

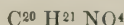
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\*  $\frac{\gamma}{\delta\rho\epsilon\zeta\iota\sigma}$ , appetite.

Orexin hydrochlorid and zinc dust are heated over the flame in a glass tube (isonitril reaction). Bleaching powder ( $\text{Ca OCl}^2$ ) solution gives a blue color to the filtered liquid when the residue has been treated with diluted (1:1) hydrochloric acid (anilin reaction).

(g) It leaves no residue when ignited on platinum foil.

### **Papaverin.**



A crystalline powder, melting at  $147^\circ$ , without coloring; solidifies again to crystals, while cooling; if heated higher, it becomes greenish-yellow colored, chars, and gives off alkaline vapors. Papaverin has no action on litmus paper; its salts have an acid reaction. A saturated watery solution of it is tasteless; its sulfate tastes rather pungent than bitter. Is easily soluble in acetone, alcohol and chloroform; less so in ether and carbon disulfid; in water it dissolves with difficulty, even by long continued boiling. —Crystalline needles form, however, in the filtrate, when 0.020 g. Papaverin has been boiled with half a liter water.

(a) Reagents 6, 7 and 12 give a slight turbidity in the mother liquor of these crystals. Reagents 11, 13, 14, 16, 17, 19 and 24 give no reaction.

(b) It colors lilac when strewn upon sulfuric acid (Reagent 21); this color is more brown-red, if a particle of sodium nitrate ( $\text{Na NO}^3$ ), or a trace of nitric acid (Reagent 15), has been added to the sulfuric acid. Sulfuric acid, strictly free from nitrogen compounds, shall not give a color with Papaverin (Hesse 1886), this color reaction being due to Papaveramin.

(c) Sulfuric acid gives a brown-black color reaction, afterwards turning red, when a mixture of equal parts of sodium nitrite ( $\text{Na NO}^2$ ) and Papaverin is strewn upon it.

(d) Papaverin colors Reagent 22 brown, slowly.

(e) It becomes dark brown to bluish-black colored when chlorin water (Reagent 3) is poured over it. It sinks in yellow-brown streaks to the bottom, when it is strewn upon chlorin water (Reagent 3); the whole liquid colors brown, when seen in a white bottle.

(f) It gives a brown color reaction if treated with bismuth subnitrate, as described under article *Morphin*, page 76; molybdic, titanio and tungstic acids give lilac-colored reactions.

(g) 0.010 g. Papaverin dissolves colorless in one (1) c. c. of nitric acid (Reagent 15); this solution colors yellow in course of time—sooner by warming; yellow crystals of nitro-Papaverin nitrate ( $C^{20}H^{20}(NO^2)O^4$ ,  $NO^3H+H^2O$ ) form after a few hours. The experiment can be made so that they are very little soluble in boiling water, if this reaction is carried out in a test tube. Papaverin does not give the reaction described for *Morphin* under “(g),” “(h)” and “(m),” page 77.

(h) It is very little soluble in lime water.

(i) Chlorin water (Reagent 3) acts upon a solution of Papaverin sulfate in water, 1:50, as on the free alkaloid.

(j) Reagents 11, 13, 14, 16, 17, 19 and 24 give precipitates in the watery solution of a Papaverin sulfate.

(k) Nitric acid (Reagent 15) precipitates a white nitrate in the sulfate solution that is soluble in an excess of the acid; amorphous at first, it becomes crystalline in the course of an hour, forming large, shining crystals of the monoclinic system. Fine, yellow, crystalline needles form, however, if the colorless fluid, together with the amorphous precipitate, or with the colorless crystals, is warmed on the water bath and allowed to cool.

(l) Many salts, in concentrated solutions, liberate the alkaloid from a solution of Papaverin sulfate; *e. g.*, ammonium oxalate, potassium iodid, Rochelle salt, sodium acetate, nitrate and phosphate; Oxalic acid, too. The turbid fluid becomes clear in course of half a day, and Papaverin or its salts soon form crystals.

### Paracotoin.



A tasteless, crystalline powder of faint yellow color, melting at about 152°, whereby it colors brown and sublimes. Very soluble in chloroform; also soluble in ether, alcohol and carbon disulfid.

(a) A faintly yellow, neutral fluid is obtained when 0.10 g. of Paracotoin is boiled for a while with one hundred (100) c. c. of



water; this solution is hardly bitter, and ferric chlorid solution (Reagent 4) does not give any color to it—(see *Cotoin*, page 43); lead acetate solution causes no precipitate; white, crystalline needles form soon, if the fluid is allowed to cool.

(b) Ferric chlorid solution (Reagent 4) does not affect its alcoholic solution.—Compare *Cotoin*, page 43.

(c) Ammonia water (Reagent 1) does not color it yellow.

(d) It gives a greenish-brown color reaction with sulfuric acid (Reagent 21), which darkens, when sodium nitrite ( $\text{Na NO}^2$ ) has been added.

(e) It is soluble in nitric acid (Reagent 15) with a permanent bright yellow color.

### **Paraldehyd.**



A liquid ( $15^\circ$ ) of a somewhat ethereal odor and a sharp pungent taste. Sp. gr. 0.998. Boiling point  $123.5^\circ$ . It is converted into aldehyd when distilled with sulfuric acid, to be recognized by its irritating odor, and by its property of reducing silver from a silver nitrate solution.

(a) Is solid and crystalline at  $10^\circ$ .

(b) Paraldehyd is miscible at the normal temperature in all proportions with alcohol, ether, chloroform, carbon disulfid, liquid paraffin and benzene.

(c) Paraldehyd is clearly soluble in ten (10) times its volume of water at  $15^\circ$ ; this solution becomes turbid when slightly warmed; clears up when allowed to cool; has a very slight acid reaction to litmus.

(d) It can be mixed with nitric acid (Reagent 15) without decomposition.

(e) A mixture of one (1) c. c. of sulfuric acid (Reagent 21) and five (5) drops Paraldehyd, soon becomes brown-colored.

(f) A greenish-yellow color reaction, soon changing to brown and black, takes place when one (1) drop of Paraldehyd is carefully spread out on a porcelain lid and a few drops of sulfuric acid (Reagent 21) added; a violent action takes place when larger quan-

tities of Paraldehyd and sulfuric acid are added together; the mixture chars.

(g) Caustic soda has no action upon Paraldehyd—remains white.

(h) Paraldehyd does not immediately reduce silver from a solution of  $\text{Ag NO}_3$ , neither in the cold or by warming—only after a while.

### **Pelletierin Tannate.**

The commercial article is a mixture of the tannates of the total alkaloids from *cortex punicæ granati* (pomegranate bark).\* Is an amorphous, pale, yellowish-gray powder of an adstringent taste, soluble in warm dilute acids and in alcohol; hardly in water.

(a) Litmus paper shows a faint acid reaction. Lime water gives a greenish-blue precipitate; ferric chlorid solution (Reagent 4) a bluish-black precipitate, in the filtrate of a mixture of 0.010 g. of the preparation with five (5) c. c. water;—Reagent 12 gives a reaction on alkaloids in this filtrate.

(b) Red litmus paper does not become blue when it is kept near the surface of a mixture of one (1) g. of the preparation, 0.050 g. slacked lime, and ten (10) c. c. of water.

(c) Chloroform (or ether) leaves, on evaporation, a few colorless drops of an alkaline reaction, when agitated with the mixture described under “(b)”. These drops have a peculiar odor and are nearly tasteless. Pelletierin is a liquid alkaloid of a somewhat aromatic odor.

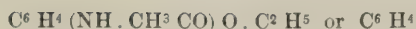
(d) The alkaline drops also give white clouds from a glass rod moistened with hydrochloric acid.

(e) Reaction 12 gives an abundant precipitate, if this residue from ether or chloroform is dissolved in two (2) c. c. of water. This precipitate sinks quickly to the bottom, becomes granular and yellow colored. Reagent 13 gives only a turbidity in it.

The most valuable identity reaction, however, is its applicability as a tænicide (against tapeworm). Negative results will have to be verified and corrected accordingly.

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\**Cortex Punicæ grana'i* contains four (4) alkaloids. Compare Husemann and Hilger, *Die Pflanzenstoffe*, II, page 993. Berlin, J. Springer, 1884.

**Phenacetin.**

## PARA-ACETPHENITIDIN.

Odorless and tasteless, small, crystalline laminæ. Melting point 135°; it solidifies again to crystals, if allowed to cool after being melted; it gives off odorless, white vapors, when heated higher, condensing to crystals by cooling. Ignited on platinum foil it leaves no residue.

Soluble in alcohol of ninety-four (94) per cent., at 20°, 1:16; in ether, at 20°, 0.5:100 parts; in chloroform at 20°, 3.3:100; much less in carbon disulfid. In water at 100°, 1:70, at 20° 1:2000.\*

Shining crystals form when the warm saturated solution is allowed to cool. Phenacetin does not liquify to drops when it is boiled with a quantity of water insufficient to dissolve it, as Methacetin does.

(a) Its watery solution does not affect litmus.

(b) Neither Reagent 4 or Reagent 17 have any effect upon it.

(c) It dissolves colorless in sulfuric acid (Reagent 21) even when warmed with it on the water bath and a trace of Reagent 4 is added. In warm sulfuric acid it dissolves, often with a blue color; this blue color may be due sometimes to an impure acid.

(d) It dissolves in *cold* nitric acid (Reagent 15) with an orange color,—difference from acetanilid and antipyrin, on which cold nitric acid has no effect.

(e) 0.10 g. Phenacetin is dissolved in two (2) c. c. of hydrochloric acid (Reagent 5) only by warming; this solution becomes turbid on addition of eight (8) c. c. of water, but clears up again on warming. It becomes purple colored on addition of one (1) drop of Reagent 17; bright red, on addition of one-half (0.5) c. c. of Reagent 4,—this color soon changes, however, to a dirty green. Five (5) c. c. of hydrochloric acid (Reagent 5) does not dissolve

\*A certain quantity of water, agitated uninterruptedly, in an automatic shaker, with an excess of Phenacetin that answered to all the tests for purity, for ten (10) hours, in our laboratory, dissolved 0.027 g. in fifty (50) c. c. It has been found to require 1:1400 to 1:1500 by others.—[J. B. N.]

0.10 g. Phenacetin, at 15°—difference from Methacetin, which dissolves in the acid in these proportions.

(f) 0.50 g. Phenacetin dissolves, when added to two (2) g. chloral hydrate previously melted on the water bath (100°); and the solution is colorless if the Phenacetin is free from paraphenetidin; it is intense violet colored, if the paraphenetidin impurity is present. Sensitive on 0.00066 paraphenetidin (Reuter).\*

In course of ten hours or less, the solution becomes slightly rose-colored.

(g) A dark violet colored solution, which turns green in a few hours, is obtained if 0.030 g. Phenacetin is triturated with an equal part of sodium nitrite ( $\text{Na NO}^2$ ), and this mixture strewn upon one (1) c. c. sulfuric acid (Reagent 21). The color reaction is immediately green when sodium nitrate ( $\text{Na NO}^3$ ) is substituted for the nitrite; the green color soon turns brown.

(h) An odor of ethyl acetate is liberated by warming, from a mixture of 0.50 g. Phenacetin, one (1) c. c. of alcohol of ninety-four (94) per cent., and two (2) c. c. sulfuric acid (Reagent 21).

(i) An odor of phenylisocyanid is liberated when 0.20 g. Phenacetin is boiled for a while with five (5) c. c. of a ten (10) per cent. caustic soda solution, the fluid allowed to cool, 0.020 g. chloral hydrate added, and the mixture warmed again.—Compare *Acetanilid*, page 1.

(j) A brown-yellow paste of crystalline nitrophenacetin ( $\text{C}^{10}\text{H}^{12}(\text{NO}^2)\text{O}^2$ ) is obtained when 0.20 g. Phenacetin is triturated with two (2) c. c. nitric acid (Reagent 15); hardly any heat develops thereby. The crystals dissolve in fifty (50) c. c. of water at 100° forming a yellow-red solution; and bright yellow crystal needles form, if the solution is allowed to cool, that do not give an acid reaction to litmus paper, if properly washed with water; they dissolve in an alcoholic caustic soda solution, with intense red color.—Compare a similar reaction described for *Methacetin*, page 74.

(k) Shining, red-brown crystals form if two (2) c. c. of Reagent 7 and one (1) c. c. hydrochloric acid (Reagent 5) are added to seven (7) c. c. of a saturated aqueous solution (15°) of Phenacetin.

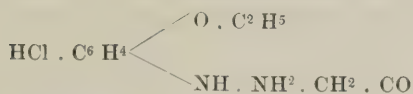
(l) A red-brown colored fluid is obtained in the course of half an hour when five (5) drops of ammonia water (Reagent 1) are

\* "We lay stress upon the importance of this reaction for the pharmaceutical chemist; paraphenetidin being poisonous." (Reuter).

added to ten (10) c. c. of a saturated (15°) watery solution of Phenacetin, previously diluted with an equal volume of chlorin water (Reagent 3).—Compare *Methacetin*, *Morphin*, and *Quinin*.\*

(m) Ferric chlorid solution (Reagent 4) proves the presence of salicylic acid with its peculiar purple-violet color reaction, in a filtrate from a mixture of 0.010 g. Phenacetin and two (2) g. zinc dust (previously heated in a glass tube until it commenced to char) and agitated with three (3) c. c. of water.—Compare a like reaction described under *Methacetin*, page 74, and *Phenocollhydrochlorid*.

### Phenocoll Hydrochlorid.



AMIDOACETPARAPHENITIDIN, HYDROCHLORID, GLYCOLLIPARAPHENITIDIN.

A crystalline powder of a salty, with a sweet after-taste, possessing an aromatic odor. Soluble 1:16 in water at normal temperature, in much less at 100°, these solutions having no reaction upon litmus; colorless, short prisms form in the hot saturated watery solutions, when allowed to cool. Very soluble in alcohol; hardly so in ether; chloroform and carbon disulfid.

(a) Ammonia is liberated, when a mixture of 0.020 g. of the salt and 0.10 g. calcium carbonate is carefully heated in a glass tube. Though  $\text{NH}^3$  is *not* evolved by gently heating, it is by calcining the salt with  $\text{CO}^3\text{Ca}$ .

(b) Chars if heated to about 200°, when salicylic acid can be detected in the residue by its reaction with ferric chlorid solution (Reagent 4). Slightly heat 0.005 g. of the salt in a glass tube, shake the slightly charred mass with one (1) c. c. of water; the filtrate has an acid reaction (hydrochlorid acid).—Compare *Methacetin*, page 74, and *Phenacetin*, page 91.

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\*There is no necessity to pay much attention to the statement that "Phenacetin has an influence on the Thalleioquin reaction." But since it is recorded (Am. J. o. Ph., 1891, 483), the fact may be mentioned; it is of no importance. Thalleioquin is insoluble in ether, and the Phenacetin compound is soluble. Prof. Flückiger's preface is well worth reading again.—[J. B. N.]



(c) Reagent 7 gives in a saturated aqueous solution a voluminous precipitate, which becomes crystalline in a few hours.

(d) Reagent 2, in like solution, causes a turbidity, which soon disappears; this is made more permanent by adding twenty-five (25) c. c. of the Reagent to one (1) c. c. saturated aqueous solution of Phenocoll hydrochlorid.

(e) The precipitate obtained by the addition of four (4) c. c. of Reagent 12 to one (1) c. c. of the watery solution of the salt sinks in course of half a day to the bottom, in yellow drops.—Compare *Pilocarpin*, page 98, which gives a similar reaction.

(f) Reagent 13 gives an amorphous precipitate in same.

(g) Reagent 14 causes slight turbidity only.

(h) Reagent 19 gives a pale yellow precipitate, soon crystallizing, in same saturated aqueous solution of Phenocoll hydrochlorid.

(i) Strewn upon sulfuric acid (Reagent 21) Phenocoll hydrochlorid gives a pale yellow color reaction, which becomes darker in time; heating does not make the color more intense, but addition of sodium nitrate ( $\text{Na NO}_3$ ) or nitrite ( $\text{Na NO}_2$ ) changes to dark red-brown.

(j) With nitric acid (Reagent 15) it gives a permanent greenish-yellow color reaction. A bright red, clear solution is obtained, if 0.50 g. of the salt is heated to boiling with one (1) c. c. of the acid; a brown nitro-compound forms in crystals if this solution is allowed to cool.

(k) Large yellow crystals form, if one (1) c. c. of the saturated watery solution of the salt is diluted with nine (9) c. c. of water, and one (1) c. c. of Reagent 16 is added.

(l) Yellow, crystalline laminae form, when two (2) c. c. of the saturated watery solution of the salt is mixed with one (1) c. c. of Reagent 17.

(m) Neither ammonia water (Reagent 1), caustic soda solution (Reagent 20), tannin solution (Reagent 24), or ferric chlorid solution (Reagent 4), cause any turbidity or color reaction in the watery solution; turbidity or a color reaction evidences impurity.

(n) Lead acetate and  $\frac{\text{N}}{10}$  silver nitrate solutions give precipitates; copper is reduced from cupric to cuprous oxid in an alkaline copper tartrate solution by it.\*

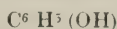
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\* Prepare an alkaline copper tartrate solution as directed on page 4.

(o) A mixture of one (1) c. c. of the watery solution of the salt and one (1) c. c. of a copper sulfate solution (1:14) solidifies to a crystalline mass of Phenocoll hydrochlorid.

(p) An amorphous yellow precipitate is thrown down, in a boiling solution of 0.050 g. of the salt, by the addition of 0.10 g. sodium nitrite ( $\text{Na NO}^2$ ) and 0.10 of mercuric chlorid in five (5) c. c. of water.

### Phenol.



A colorless crystalline mass, composed of long needles, melting at  $44^\circ$ , when crystallized from petroleum ether; from other menstrua, it melts at  $42^\circ$ . Boiling point  $180^\circ$ ; its vapors are combustible. Melted Phenol makes filter paper transparent; it evaporates, however, entirely, when slightly warmed.

Phenol has a not disagreeable odor, sweetish, aromatic—not creasot-like; a sweet taste, if dissolved 1:100 in water, with a burning after-taste. Soluble in *one* to *fourteen* (1:14) parts of water at  $15^\circ$ , and with a slight acid reaction to litmus. At  $87^\circ$  it is miscible with water in all proportions, and sinks to the bottom in drops if the solution is allowed to cool.

Easily soluble in ether, benzene, chloroform, absolute alcohol glycerol (1:4) carbon disulfid, glacial acetic acid, and in caustic alkalies; in caustic ammonia 1:2, when slightly warmed. Coagulates albumen, also pyroxylin in collodion; dissolves gelatin.

When exposed to moist air, it becomes colored and liquefies.\*

(a) A green fluid is obtained, when one (1) c. c. ferric chlorid solution (Reagent 4) is added to a solution of twenty (20) parts of Phenol in ten (10) parts of alcohol of ninety-four (94) per cent.; this solution remains clear after the addition of water, and colors permanent violet, if the dilution does not exceed two thousand (2,000) parts of water to one (1) part of Phenol. Ferric chlorid solution (Reagent 4) also gives the same violet color reaction in a very dilute (1:3000) watery solution.

(b) A freshly prepared solution of potassium ferricyanid

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\*Due to the presence of  $\text{H}^2\text{O}^2$ , produced during the exposure. This was proved by the titanin acid, chromic acid and ether, and potassium iodid tests.—[RICHARDSON.] J. o. t. Soc. of Chem. Ind., May 31, 1893, page 415.

(Reagent 18) gives a blue precipitate in the above obtained violet watery fluid—the Phenol has reduced the ferric salt to a ferrous compound.

(c) Lead acetate solution, ten (10) per cent., gives a voluminous, amorphous precipitate in a saturated, watery solution of Phenol. Sub-acetate of lead, or any other solution of salts of the heavy metals, does not give a precipitate.

(d) Phenol dissolves colorless in sulfuric acid (Reagent 21) in the cold—red-brown or green color reaction observed in this test may be due to a larger or smaller trace of nitric acid present as impurity of the sulfuric acid. A red color is formed when Phenol is *warmed* with sulfuric acid (Reagent 21).

(f) Phenol dissolves in nitric acid (Reagent 15) with a brown-red color.

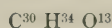
(g) Bromin vapors give a flocculent, white, precipitate of tribromphenol,  $C^6H^2Br^3(OH)$ , when they fall into a watery solution of Phenol; the solution remains colorless. Recrystallized from a hot alcoholic solution, it forms white (not very soluble) needles that melt at  $95^\circ$ , sublime easily and can be distilled unaltered; crystals form when the fluid contains only one (1) part Phenol to 57,000 of solution, tribromphenol being very little soluble. The forming of crystals is the only characteristic part of the reaction, because bromin vapors give precipitates with many other substances, *e. g.*, with benzene derivatives, alkaloids, aloin and glue.

(h) A permanent blue, or bluish-green color reaction takes place when bromin vapors fall upon a mixture of five (5) c. c. of ammonia water, and fifty (50) c. c. of a watery Phenol solution. This blue color is insoluble in ether, and in chloroform. Chloroform becomes red tinged, when agitated with the mixture. The blue solution is soluble in alcohol with a green color; a red residue is obtained, changing to blue, by addition of ammonia water (Reagent 1), when this alcoholic solution is evaporated to dryness. Acids change the blue color to a red, in which condition it is soluble in ether; ammonia water (Reagent 1) causes the blue color to appear again; water takes it out from the ethereal solution. The blue color appears with vapors of bromin when a test tube is moistened with a solution of 0.001 g. Phenol in twenty (20) c. c. of water.

(i) Far less sensitive color reactions are obtained if bromin

water (instead of bromin vapor) is used and this added to an ammoniacal or a saturated watery solution of Phenol to which an equal volume of ammonia water (Reagent 1) has been added.

### **Picrotoxin.**



Forms crystalline needles. Melting point  $201^{\circ}$ . Soluble in water ( $15^{\circ}$ ) 1:400, the solution being intensely bitter, with no reaction on litmus; caustic potash, soda, or ammonia solutions ten (10) per cent. dissolve it easier; also soluble in glacial acetic acid and in alcohol; less soluble in ether, or chloroform ( $15^{\circ}$ ).

(a) Dissolves in sulfuric acid (Reagent 21) to a yellow-brown, fluorescent fluid (changing to red-brown in the course of a day) in which water does not cause turbidity as in a phosphoric acid solution.

(b) A green-yellow color reaction is obtained when equal parts of Picrotoxin and caustic soda are moistened with a drop of water; the green color changes to red-brown.

(c) It dissolves colorless in nitric acid (Reagent 15), even on warming.

(d) A bright red color reaction is obtained with Picrotoxin as follows: Add one (1) drop sulfuric acid (Reagent 21) to 0.005 g. sodium nitrate ( $\text{Na NO}_3$ ); spread out on a porcelain lid; strew a mixture of 0.050 g. Picrotoxin and 0.050 g. sodium hydrate ( $\text{Na OH}$ ) in the midst thereof; stir with a glass rod moistened with alcohol or water.

(e) The particles of Picrotoxin becomes dark red to violet-colored, if reaction "(d)" is modified, so that 0.005 g. Picrotoxin and 0.050 g. sodium nitrate ( $\text{Na NO}_3$ ) are taken; the color fades in the course of an hour; more alcohol does not prevent this.

(f) Picrotoxin (0.020 g.) reduces in half an hour in the cold, quicker by warming, a diluted alkaline cupric tartrate solution (0.5 c. c. solution to 2.5 c. c. cold water). Reduces also an ammoniacal  $\frac{N}{10}$  silver solution.

(g) A mixture of equal parts sugar and Picrotoxin is colored red by the addition of sulfuric acid (Reagent 21).

(h) A brown fluid is obtained when ten (10) c. c. diluted phosphoric acid (1.154 sp. gr.) is concentrated on the water bath and a few particles of Picrotoxin added thereto; addition of water causes a brown flocculent sediment; the filtrate is yellow.

(i) A few drops of ferric chlorid solution (Reagent 4) gives a red-brown color in the colorless, neutral, filtrate, obtained from a mixture of 0.020 g. Picrotoxin, 0.020 g. magnesium carbonate, and twenty (20) c. c. of water, that has been boiling for an hour and the water lost by evaporation replaced; this color fades on addition of hydrochloric acid (Reagent 5).

### **Pilocarpin.**



Exceedingly hygroscopic and therefore very difficult to obtain in crystals. The amorphous mass is easily soluble in ether, alcohol, chloroform and water, which solutions give no alkaline reaction towards litmus, but are plainly alkaline to cocceionella tincture.

Pilocarpin hydrochlorid forms crystalline laminæ of an acid reaction (probably due to a dissociation) to litmus. Is easily soluble in water and alcohol; the watery solution, 1:50, tastes faintly bitter. Neither nitric or sulfuric acids (Reagents 15 and 21) give any color reactions with this salt.

(a) A characteristic reaction, had in common with cocain, is that Pilocarpin reduces calomel to Hg (blackens it), when 0.010 g. of the alkaloid or the hydrochlorid and one (1) g. mercurous chlorid are triturated together and moistened by the breath. It cannot be mistaken for cocain.—Compare *Cocain*, page 34.

(b) Another somewhat peculiar reaction is the behavior of the precipitate obtained from Reagent 12 in a diluted solution of the hydrochlorid; the amorphous precipitate sinks to the bottom, in the course of a day, in oily drops.—Compare, however, *Phenocoll hydrochlorid*, page 94.

(c) Reagent 7 gives, in Pilocarpin solutions, a brown precipitate that often crystallizes to feathery brown crystals (microscopi-



cally), and of serrated form, something like the blade of a scroll saw, when the crystallization is incomplete.

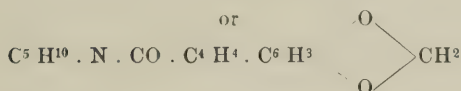
(d) Reagents 2, 6, 7, 13, 14 and 17 give precipitates in the watery solution of Pilocarpin salts (1:50); but Reagents 16, 22 and 24 do not. The alkaloid and its salts are clearly soluble in Reagent 11. A brown precipitate, which crystallizes partially in a day, is given by Reagent 7 in an excess of a solution of Pilocarpin. If one (1) volume of the Reagent is mixed with two (2) volumes of the solution (1:50), feathery black crystals are formed in abundance.

(e) Pilocarpin salts increase the secretion of saliva, tears, bronchial sputa, perspiration; decrease the heart-beat; produce myosis.\*

### Piperin.

$C^{17} H^{19} NO^3$  (like Morphin)

or



Crystallizes in prisms of the monoclinic system. Melting point  $129^\circ$ , whereby it becomes a yellow fluid, that solidifies like glass, on cooling—it can be brought to recrystallization, when this slack is warmed on a water bath; it chars when heated higher and gives off vapors of an alkaline reaction. It has a lasting, sharp, hot taste, especially in an alcoholic solution. Soluble in acetone, ether, alcohol, benzene, chloroform and carbon disulfid; also in warm acetic acid, giving a yellow-colored fluid, from which it separates into drops, when allowed to cool. Water causes milky turbidity in the acetic acid solution, and the Piperin forms delicate crystals. Reagent 12 makes the filtrate opalescent.

It can be recrystallized in needles from the watery solution, if 0.050 g. Piperin is boiled for a while with one-half (0.5) liter of

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\*Pilocarpin hydrochlorid often contains Jaborin as an impurity, in which case it increases the pulse, causes thirst and mydriasis, and a dry skin. Jaborin is a powerful antagonistic. The composition of Jaborin is unknown.—R. Kobert, *Lehrbuch der Intoxikationen*, page 622. Stuttgart, Ferdinand Enke, 1893.

water and the fluid allowed to cool—a trace of Piperin remains hereby in solution; this has a hot taste and is sensitive to Reagents 6 and 7, but not to Reagent 12.

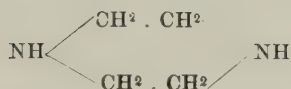
(a) Piperin 0.001 g. dissolves in five (5) drops sulfuric acid (Reagent 21) with a yellow color, changing immediately to a red; on being breathed upon it fades to a greenish-yellow.

(b) Piperin colors yellow-red when strewn upon nitric acid (Reagent 15); the acid itself colors yellow.

(c) The addition of a trace of sodium nitrite ( $\text{NaNO}_2$ ) to its acetic acid solution, gives a red color reaction.

(d) Acts with bismuth subnitrate like morphin—(compare *Morphin*, page 76), with the difference, however, that the black color is preceded, for a moment, by a yellow-red color; Piperin, recrystallized from water, gives this yellow-red color only. Similar results are obtained if the bismuth subnitrate is substituted by ammonium molybdate, titanio acid, or a tungstate—the color obtained from titanio acid is more of a lilac color.

### Piperazin.



DIETHYLENDIAMIN. HEXAHYDROPYRAZIN.

Forms a crystalline mass of prismatic crystals, of a faint, peculiar odor, and a taste suggestive of saltpetre and salmiak. Melting point  $107^\circ$ . Boiling point  $146^\circ$ . It sublimes entire. Is very hygroscopic, and attracts carbonic acid from the atmosphere, whereby it liquefies to a carbonate. Has an alkaline reaction to litmus and phenolphthalein. Is easily soluble in water, which solution [five (5) per cent.] decomposes calomel; freely soluble in alcohol; less so in ether,—soon forms crystals in an ethereal solution—but the alcoholic solution is not precipitated by ether; it liquefies in chloroform, but does not dissolve much; is clearly soluble in lime water (Reagent 10), without liberating  $\text{NH}_3$ .

(a) Hydrochloric acid (Reagent 5) gives off dense white clouds when a glass rod, moistened with a ten (10) per cent. Piperazin solution, is held close to it.

(b) Reagents 2, 6 and 7 cause a turbidity in a watery solution 1:100; Reagent 6 in large excess. The turbidity caused by Reagent 12 crystallizes in course of half a day; so sometimes do the precipitates caused by Reagents 11, 12, 13 and 14 in a watery solution (1:100).

(c) Reagent 16 gives a crystalline precipitate, even in a watery solution of 1:200.

(d) Reagent 24 gives an amorphous precipitate in same.

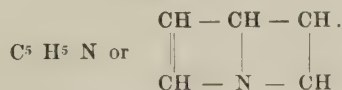
(e) A five (5) per cent. solution of Piperazin precipitates the respective hydroxides from five (5) per cent. alum-, magnesium-, zinc-, ferrous- and copper-sulfate solutions. The filtrate is alkaline, when an excess of Piperazin is added to the copper sulfate solution; the precipitate does not dissolve.

(f) Piperazin hydrochlorid crystals form, when alcohol is added to its solution in hydrochloric acid (Reagent 5).

(g) Sulfur is liberated from carbon disulfid, when Piperazin is triturated therewith. Water gives a neutral filtrate, when the residue from the evaporation of the CS<sup>2</sup> is treated with it; Reagents 11, 12, 13 and 14 give precipitates in this watery solution. Piperazin no longer acts in like dilution upon alum—or magnesium sulfate solutions; it gives brown precipitates now with ferrous and copper-sulfate solutions.

(h) Reagents 22 and 23 act very slowly on Piperazin.

### Pyridin.



A colorless, very mobile fluid, permanent in the light; of a strong, persistent, and to most people disagreeable odor, readily detected in large dilutions; a burning, aromatic, not permanent bitter taste; very hygroscopic. Sp. gr. at 15°, 0.980. Boiling point 116.5°.\*

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\* M. P. Cazeneuve, Journal de Pharmacie et de Chimie xxvi, page 199, 1892.

Hydrochloric acid gives white clouds when brought near to it.—Compare *Anilin*, page 8. Is highly inflammable, and burns with a sooty flame. Dissolves easily in water, which solution has a strongly alkaline reaction to litmus, but not to phenolphthalein, *when strictly pure*—commercial articles often produce in one (1) per cent. dilutions, however, a pink color with a few drops of 1:100 alcoholic phenolphthalein solution, that is probably due to the presence of ammonia. Miscible with ether, alcohol, liquid paraffin and benzene; also with lead acetate solutions, 1:10.

(a) Pyridin gives a brown turbidity in Reagent 6 which soon clears up; small, brown, crystalline needles form in the fluid, by which the latter is decolorized.

(b) Reagent 7 solidifies, upon the addition of Pyridin, to a crystalline magma.

(c) Reagents 2 and 12 give voluminous precipitates in a ten (10) per cent watery solution of Pyridin.

(d) Reagents 12, 13 and 14 give precipitates that soon become crystalline. Reagents 2 and 13 are most sensitive to Pyridin; Reagent 12 the least so.

(e) No precipitate is caused by Reagent 19, even after the addition of hydrochloric acid; neither have Reagents 16 and 17 any effect upon Pyridin solutions. Reagent 16 throws down, however, a crystalline precipitate, when added to a strong solution of Pyridin salts.

(f) A two (2) per cent watery Pyridin solution precipitates the hydroxides completely, in five (5) per cent. alum-, ferrous-, and zinc-sulfate solutions—these filtrates have an alkaline reaction; it does *not* give a precipitate in a five (5) per cent. magnesium sulfate solution.—Compare *Anilin*, page 7.

(g) Reagent 24 gives a heavy precipitate in a two (2) per cent. watery Pyridin solution.

(h) Pyridin gives a turbid mixture when agitated with an equal volume of a watery solution of magnesium sulfate, 1:10; this mixture separates into two clear layers—a large top layer and a smaller under one.

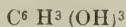
(i) Pyridin causes a precipitate of  $\text{SO}_4 \text{ Cu} (\text{C}_5\text{H}_5\text{N})_4$ , in a watery copper sulfate solution (1:15), which dissolves with a blue color in a slight excess of the precipitant, acting like ammonia. The copper compound can be recrystallized from hot water.

(j) Pyridin does not give a precipitate in a silver nitrate solution (1,7:100).

(k) Calomel blackens, when agitated with Pyridin; white needles very soon form in the flask, probably of the composition  $(C^5H^5N)^4 HCl + HgCl^2$ , when recrystallized from boiling water. Neither potassa, soda or caustic-ammonia solutions give precipitates in the solutions of Pyridin salts. Sodium converts Pyridin largely into dipyridin ( $N^2C^{10}H^{10}$ ), partially into isodipyridin; the former crystallizing in odorless needles melting at  $108^\circ$ , soluble in ether, alcohol and in boiling water; isodipyridin, on the contrary, is not soluble in water, but it mixes clear with ether and chloroform, boils at  $300^\circ$ , and is not known to exist in the solid form.

(l) Potassium ferrocyanid solution (Reagent 19) gives in a watery solution of dipyridin a yellow precipitate which soon turns blue.

## Pyrogallol.



### PYROGALLIC ACID.

A bulky, white crystalline powder (or thin plates) slowly subliming at water bath temperature; can be distilled only when oxygen is excluded (in a current of carbon dioxid). Boiling point  $210^\circ$ . Melting point  $131^\circ$ ;\* it solidifies crystalline again by cooling; if heated higher it chars, and partly sublimes. Soluble in water, 5:9; in alcohol of 0.83 sp. gr. 1:2; in absolute ether 5:11 parts, at the normal temperature; very little soluble in chloroform, benzene or carbon disulfid. The watery solution has an acid reaction to litmus paper; a bitter (poisonous) taste, and soon turns brown in contact with the atmosphere; this bitter taste can hardly be

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\* M. P. Cazeneuve in *Journal de Pharmacie et de Chimie*, xxvi, page 200, 1892. Sur la transformation de l'acide gallique en pyrogallol. Point de fusion du pyrogallol. "Certains échantillons de pyrogallol, impurs, fondaient à  $115^\circ$ ; d'autres, d'une grande blancheur, purifiés par sublimation, se ramollissaient vers  $115^\circ$ - $116^\circ$  et fondaient vers  $129^\circ$ - $130^\circ$ . Après plusieurs cristallisations dans le toluène, nous avons constaté que ces pyrogallols, de pureté et d'origine diverses, fondaient au delà de  $130^\circ$ . Nous estimons que le point de fusion du pyrogallol est  $130^\circ$  et non pas  $115^\circ$ , comme les livres classiques le répètent."



detected in a dilution of the strength 1:150. Pyrogallol does not decompose sodium thiosulfate—compare *Gallic acid*, page 56.

(a) Soluble in sulfuric acid (Reagent 21) with a canary yellow color, which soon disappears; 0.001 g. in two (2) drops of the acid causes brown streaks on the addition of a particle of sodium nitrate ( $\text{NaNO}_3$ ).

(b) Soluble in nitric acid (Reagent 15) with violent action and an olive-greenish-brown color—0.001 g. in one drop of the acid.

(c) A freshly prepared solution gives a brown or black precipitate in a watery copper sulfate solution (1:14) under the same conditions as described for *Gallic acid*.

(d) A clear crystal of ferrous sulfate causes in the freshly prepared, colorless, watery solution of Pyrogallol (1:10) an indigo blue color—the purer the ferrous sulfate, the lighter the blue color; this color increases in a short time, oxygen being absorbed; is more violet, when a trace of sodium acetate, or calcium carbonate, has been added to the mixture.

(e) The solution “(c)” becomes red on addition of ferric chlorid solution (Reagent 4), and  $\text{Fe}^2 \text{Cl}^6$  is thereby reduced to ferrous-chlorid  $\text{FeCl}^2$ . The blue coloration, due to the ferrous compound—see “(d)”,—appears when the hydrochloric acid, liberated by the Pyrogallol acid, has been neutralized by  $\text{CaCO}_3$ .

(f) 0.010 g. ammonium vanadate is soluble in four (4) c. c. of the Pyrogallol solution with a yellow color, soon turning dark brown.—Compare *Gallic acid*.

Pyrogallol solutions do not throw down the alkaloid in solutions of alkaloidal salts.

(g) Two (2) c. c. of the Pyrogallol solution and one (1) c. c. of ammonia water (Reagent 1) gives a bright yellow colored fluid, soon turning brown.

(h) 0.010 g. Pyrogallol dissolves in ten (10) c. c. lime water (Reagent 10) with a lilac color; the solution soon becomes turbid and turns brown and black.

(i) Borax tinges Pyrogallol solution slowly red; sodium acetate colors it yellow in course of a day.

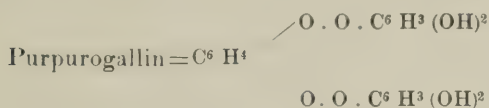
(j) Pyrogallol solution does not give a precipitate in zinc acetate solution.—It acts towards Reagent 17 like tannin.

(k) Gives white precipitates with Reagents 13 and 14; they are brown and more voluminous, in the presence of calcium carbonate.

(l) Pyrogallic acid acts like Resorcinol—compare Resorcinol page 116—with a solution of sodium nitrite ( $\text{NaNO}_2$ ) in Reagent 13.

(m) A Pyrogallic acid solution reduces silver immediately, when a  $\frac{N}{10}$  silver nitrate solution is dropped into it.

(n) Small, shining crystals of Purpuro-gallin (Pyrogalloquinon) are formed, in the course of a day, when 0.20 g. Pyrogallol and 0.870 g. Potassium ferrieyanid, each dissolved into 3.3. c. c. of water, are mixed.



### Quinidin Sulfate.



Long white needle-like crystals, giving a red tar when heated in a glass tube over the flame—not as bright red, however, as from quinin sulfate. Soluble in water, 1:100, at 15°; easily in alcohol of ninety-four (94) per cent., and in chloroform.

(a) Its saturated, watery solution is fluorescent when treated as quinin sulfate and gives the thalleioquin reaction as prescribed under article Quinin sulfate “(d)”, page 110.

(b) More than twenty (20) c. c. of lime water (Reagent 10) are needed to redissolve the precipitate caused by a few c. c. of lime water in one (1) c. c. of a saturated watery solution of Quinidin sulfate (15°); even then some flocculent calcium sulfate remains undissolved.

(c) A ten (10) per cent. KI solution gives a precipitate in the watery, saturated solution of the salt—*difference with quinin sulfate*; the alkaloid is entirely precipitated by the KI solution, if enough of the latter is added, which must be verified by ammonia water (Reagent 1). Ammonia water does not give a precipitate in the filtrate of quinidin hydriodid, when KI has been added in excess.

(d) Quinidin sulfate gives also the Herapathit reaction, when treated as described under *Quinin sulfate* (page 111), but less voluminous because the *compound of Quinidin is more soluble* than the quinin compound; the crystals are more *red*, than from quinin—not green or brownish-green; this can be seen in a comparative test when the two reactions are examined side by side, or when they are spread out in a thin film in a flat-bottomed evaporation dish.

### Quinin.

Anhydrous —  $C^{20} H^{24} N^2 O^2$  : Hydrate —  $C^{20} H^{24} N^2 O^2 + 3 H^2 O$

The *hydrate* melts in its water of crystallization at  $100^{\circ}$ ; the *anhydrous* melts at  $168-170^{\circ}$ , cooling to a transparent mass. Quinin crystallizes *anhydrous* from a watery solution, when this has been saturated at the boiling point; is soluble in 1:700 of water at  $100^{\circ}$ , in 1:2000 at  $15^{\circ}$ ; this latter solution has an alkaline reaction to litmus paper and coccionella tincture, but not to phenolphthalein solution. Tastes bitter in a 1:50,000 dilution. Heated in a glass tube it leaves a brown tar; when sugar, cotton, starch, or any other substance (Quinin acetate excepted) that gives off acid vapors by the dry distillation has previously been added, it gives instead a *carmine-red* tar, condensing in the higher and cooler parts of the test tube; this "tar" is soluble in alcohol and chloroform, is of bright red color and not soluble in ether. Quinin leaves a spongy charcoal, which ignites with difficulty when heated in a crucible.

Quinin *hydrate* is easily soluble in alcohol, ether (1:18), chloroform and carbon disulfid; less so in benzene and in liquid paraffin.

(a) No change in the physical properties of the fluid is noticed, when one (1) drop of diluted (1:10) hydrochloric acid is added to ten (10) c. c. of a saturated watery Quinin solution; the fluid becomes fluorescent, however, if diluted nitric (1:10) acid is substituted for the hydrochloric. Arsenious as well as boric, hydrofluoric, sulfuric and tannic acids cause a fluorescent fluid; HCl, HBr, HI do not, if added to a Quinin solution. The fluorescence disappears, when potassium ferrocyanid or sulfocyanid, a solution

of salmiak, of sodium acetate, of potassium bromid, or of potassium iodid is added; solutions of mercuric bromid, mercuric chlorid or mercuric cyanid are an exception.

The fluorescent property of Quinin salts is a reaction sensitive to 1:100,000, under common circumstances of good daylight, and in small quantities of fluid; at 1:200,000 in large quantities of fluid. It can best be detected when, by the aid of a magnifying glass, a bundle of rays of direct sunlight are passed through a two hundred and fifty (250) c. c. beaker filled with the dilution to be examined and placed on a piece of black paper.—Compare *Cinchonidin sulfate* (page 32), and *Cinchonin sulfate* (page 33). This property of yielding blue, fluorescent, solutions is not only shared by Quinidin, as stated, but by *Æsculin* especially, and in a more or less degree by various other substances; *Æsculin* shows the reaction in faintly alkaline solutions, the alkalinity of river water being sufficient.

(b) Precipitates are given in a watery solution of Quinin by Reagents 2, 6, 7, 12, 13, 14 and 16, but not by Reagent 17 ( $\text{Cr}^2\text{O}^7\text{K}^2$ ).

(c) Acidulated watery solutions give, with strong chlorin water (Reagent 3), red, green and blue color reactions, when the free acid is saturated. Dissolve 0.010 g. Quinin in ten (10) drops of sulfuric acid (Reagent 21); add to this exactly 0.001 g.  $\text{KClO}^3$ ; dilute carefully with two (2) c. c. of water; add drop by drop three (3) c. c. ammonia water (Reagent 1). The thalleioquin reaction. The foregoing mixture colors red if neutralized with ten (10) per cent. of dilute sulfuric acid. A red colored mixture is also obtained, when a drop of potassium ferrocyanid or ferriecyanid solution [five (5) per cent.] is previously added to the two (2) c. c. of water used to dilute the previous mixture of Quinin,  $\text{HSO}^4$  and  $\text{KClO}^3$ .

The thalleioquin reaction is also obtained when 0.050 g. Quinin, 0.10 g. of bleaching powder ( $\text{CaOCl}^2$ ) twenty (20) drops of hydrochloric acid, and one hundred (100) c. c. of water, are triturated together, ammonia water (Reagent 1) being subsequently added to the mixture. Thalleioquin is soluble in alcohol, but not in chloroform or ether; its composition is unknown. Another way to obtain it is: By first adding one (1) c. c. of sulfuric acid (Reagent 21), and next one-half (0.5) c. c. of water, to a mixture of 0.020 g. Quinin and 0.020 g. potassium chlorate ( $\text{KClO}^3$ ). Thalleioquin forms at the bottom of the test tube if a few drops of this yellow mixture



fall into two (2) c. c. of ammonia water (Reagent 1), previously diluted with an equal volume of water; the mixture becomes red, when the ammonia is saturated with diluted sulfuric acid; the addition of more ammonia water restores the green color.—These reactions do not succeed as well with potassium bromid, notwithstanding that bromin water (Reagent 2) gives a thalleioquin reaction, if substituted for the chlorin water (Reagent 3).—See *Quinin sulfate*, page 110. The thalleioquin reaction is sensitive to Quinin 1:20,000.

(d) *Anhydrous* Quinin dissolves in cold sulfuric acid (Reagent 21) with a yellow color; the solution has no fluorescence.

### Quinin Hydrochlorid.



Loses its water of crystallization, nine (9) per cent., easily by warming below 100°—the commercial article, when found with six (6), seven (7), or eight (8) per cent. water of crystallization has lost it by being exposed to the air; it melts thereby to a slightly yellow colored mass. If further heated, it becomes red-brown, gives the same red tar as described under Quinin, and an aromatic odor. Soluble in three (3) parts of alcohol of ninety-four (94) per cent.; in thirty-four (34) parts of water at 15°; in one part at 100°; insoluble in ether. A watery saturated solution (15–20°) has no fluorescence, but this appears when the solution is diluted with fifty (50) times its volume of water; it becomes more prominent, when another fifty (50) volumes of water are added and the fluid is observed under the conditions described under *Quinin*. One (1) drop of nitric acid (Reagent 15) or of sulfuric acid (Reagent 21) causes in the weaker solution a strong fluorescence, which disappears on the addition of hydrochloric acid. Quinin hydrochlorid dissolves colorless, or only faintly yellow, in Reagents 15 and 21.

0.60 g. Quinin hydrochlorid, three (3) c. c. ether, and one-half (0.5) c. c. ammonia water (Reagent 1), after being shaken together, give a clear mixture that gelatinizes in course of half a day in a closed tube.



It gives the thalleioquin reaction just as readily as the free alkaloid.—N. B. Morphin salts prevent the thalleioquin reaction. Any Quinin salt, mixed with a larger quantity of a morphin salt and dissolved in a *little* water, fails to give it.\* Compare *Morphin*. Morphin and salts of Morphin give a brown color reaction with chlorin water (Reagent 3) and Ammonia water (Reagent 1). The green color reaction, due to Quinin, will become more prominent, and the brown color reaction, due to Morphin, will fade, when the mixture of the salts is diluted with a *larger* quantity of water.

The green color appears somewhat more prominent if more water is taken.

### Quinin Sulfate.



NEUTRAL QUININSULFATE. DIQUININSULFATE.

Melts with a yellow color in its own water of crystallization when carefully heated in a glass tube over the open flame—it soon becomes red colored, however; a carmin-red solution is obtained if the melted mass is allowed to cool, and warmed with alcohol. It forms long, flexible, silky, white needles (voluminous, bulky, light), or short (heavy) crystals, according to the process of crystallization.

At 100° it loses all its water of crystallization.

It effloresces easily.—Compare *Quinin hydrochlorid*. Soluble 1:800 in water at 15°; 1:25 at 100; in glycerol, sp. gr. 1.25, 1:25 at 75°, which solution remains clear if allowed to cool; in 1:100 parts of alcohol of 0.83 sp. gr. at 15°, and in 1:5 at 75°. Traces of anhydrous Quinin sulfate, are soluble at 15° in chloroform free from alcohol; chloroform, containing one (1) per cent. alcohol (Pharmacopœal chloroform) dissolves at 18°–20°, 0.12 parts of the commercial salt (14 per cent. of water), and ten (10) parts of a mixture of one volume of absolute alcohol, and two volumes of chloroform, dissolve one (1) part of the salt. Pure ether dissolves traces of it—0.010 g. in

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\*A similar occurrence—that one alkaloid prevents a certain reaction of another—is noticed for Strychnin and Atropin—see page 136.

100 g. of ether. [J. B. N.] One (1) part of the salt, mixed with three (3) parts of magnesia or slacked lime, and heated in a test tube over the flame, does *not* give a *red*, but a brown colored tar. Its saturated watery solution, 15°–20°, is slightly fluorescent—to be seen as described under *Quinin*, page 107; this property disappears, when the solution is diluted with one hundred (100) times its volume of water; reappears upon the addition of one (1) drop of nitric or sulfuric acids (Reagents 15 or 21). The solution is very slightly alkaline to sensitive litmus paper, and to a methyl-orange solution 1:1000; not to a phenoptalein solution 1:100.

(a) Quinin sulfate dissolves in nitric or sulfuric acid, even when warm, either colorless or only with a very slightly yellow color—compare *Morphin*, page 75.

(b) The salt hardly colors, or very slightly, when agitated with chlorin water (Reagent 3); it very slowly takes a brown color—compare *Morphin hydrochlorid*, page 79.

(c) Quinin sulfate solutions mix clearly with lime water, as follows: Add lime water (Reagent 10) slowly, one (1) c. c. at a time, to three (3) c. c. of a saturated, watery solution of the Quinin sulfate under examination;—an excess—one (1) g.—of the salt is thereto agitated for an hour in a flask, with twenty-five (25) c. c. of water at the normal temperature, and filtered. Quinin hydrate separates out but is redissolved when six (6) or seven (7) c. c. of lime water, in all, has been added; far more lime water is needed, when the Quinin sulfate contains other alkaloids besides Quinin.—Compare *Cinchonidin sulfate*, page 32, *Cinchonin sulfate*, page 33, and *Quinidin sulfate*, page 105. *Strictly pure Quinin sulfate* requires less than six (6) c. c. of lime water to give a clear mixture. The test is in accordance with “Kerner’s” test, for which the U. S. Ph., 1882 edition, required (7) c. c. of ammonia water of 0.96 sp. gr., which are also *too much*.

(d) One (1) c. c. of the cold saturated, watery solution (20°) of the salt, gives the thalleioquin reaction by mixing with one (1) c. c. of chlorin water (Reagent 3), and then slowly adding a few drops of ammonia water (Reagent 1); the color is sea-green in this instance. Cuprein gives the same reaction. Compare “(b)”, article *Cuprein*.\*

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\* Compare the British Pharmacopœia, 1885, page 344, for Cuprein in Quinin Sulfate.

(e) A bluish-green thalleioquin reaction is obtained from the addition of one (1) c. c. of ammonia water (Reagent 1) to a mixture of one (1) c. c. of a watery solution of Quinin sulfate, one (1) c. c. alcohol of 94 per cent., and one (1) drop of bromin water, the latter to be taken with a glass rod. *No reaction is obtained when the substances are not mixed in the order named*—that is to say, the Quinin solution, alcohol and ammonia water are mixed first, and the drops of bromin water added afterwards. Fifteen (15) to twenty (20) drops of ten (10) per cent. diluted sulfuric acid changes the bluish-green color to red.

(f) Half (0.5) a c. c. of a five (5) per cent. potassium ferrocyanid solution produces a carmin red color in one (1) c. c. of the watery saturated solution of the Quinin salt to which, on a glass rod, one (1) drop of strong bromin water has been added.

(g) A distinctive characteristic test for Quinin is the insolubility in cold alcohol, ether, chloroform, or water, and the very slight solubility in boiling alcohol, of the microcrystalline precipitate of Herapathit obtained in the following reaction: Dissolve one-half (0.50) g. of Quinin sulfate in fifteen (15) c. c. alcohol of 0.83 sp. gr. diluted with five (5) c. c. of water, and acidulate the fluid with two (2) c. c. of ten (10) per cent. sulfuric acid; add to this solution a solution 0.20 g. iodine in ten (10) c. c. alcohol of 0.83 sp. gr.; warm the mixture slightly and allow to cool. Hereby forms a crystalline precipitate of dark green crystals by transmitted light, and shining with a metallic lustre when observed by reflected light; they have the formula  $(C^{21}H^{34}N^2O^2)^4 + SO^4H^2 + 2 HI + 4 I + 3H^2O$  (Herapathit). They polarize the light completely when the crystals are overlying each other, and are, therefore, black, when seen through the microscope.—Compare *Cinchonidin sulfate*, page 32, *Cinchonin sulfate*, page 33, and *Quinidin sulfate*, page 106. These crystals are somewhat soluble in acetone, and fairly soluble in methyl alcohol, from which they can be recrystallized; ammonia water (Reagent 1) decomposes them, as also does boiling water.

(h) Reagent 2, 6, 7, 11, 12, 13, 14, 17, 18 and 19 give precipitates in the saturated (15°) watery solution of the salt. Stellar groups of crystals, forming needles, appear in a short time in five (5) c. c. of the same watery solution, after the addition of half (0.5) c. c. of a five (5) per cent. potassium chromate ( $K^2 CrO^4$ ) solution.

(i) A ten (10) per cent. KI solution does not give a precipitate in the cold, saturated, watery solution of the salt.—Difference from quinidin sulfate.—Compare “(a)”, *Cinchonidin sulfate*, page 32.

### **Quinin Sulfate—Acid.**



MONOQUININ SULFATE. QUININ BISULFATE.

Soluble 1:10 in water, and 1:32 in alcohol of ninety-four (94) per cent. at normal temperature. These solutions are fluorescent.

The salt gives the thalleioquin reaction, the Herapathit reaction, the brown tar with lime, and all the less distinctive reactions for Quinin described before.

### **Quinin Tannate.**

(COMPOSITION NOT WELL DEFINED).

Gives the red tar if heated in a glass tube, as do all salts of cinchona alkaloids, and sometimes crystals of pyrogallol, if a larger quantity is taken. Is a yellow powder, very nearly tasteless, but often slightly bitter, soluble in fifty (50) parts boiling water, which solution is fluorescent, has an acid reaction, and becomes turbid when allowed to cool; the turbid, cold fluid contains so little Quinin, however, that ammonia water (Reagent 1) does not give a precipitate: Reagent 12 shows that there is an alkaloid present; and ferric chlorid solution (Reagent 4) reacts on tannin. In alcohol, in ether, or in chloroform, it is very little soluble; the alcoholic solution is fluorescent, when diluted one (1) drop to five (5) c. c. with water; ferric chlorid solution (Reagent 4) shows also the presence of tannin in the alcoholic solution. No thalleioquin reaction is obtained in the alcoholic solution. One (1) drop of bromin water (Reagent 2) and the addition of ammonia water



(Reagent 1) afterwards, gives only a red color (tannin reaction). Warm glycerol (50–75°) dissolves it 1:3. It is also soluble in dilute hydrochloric acid, by warming;\* Quinin tannate precipitates by cooling, and when the acid is neutralized; it can also be precipitated by the addition of salmiak. The thalleioquin reaction is not obtained in its watery solution,—the solution contains too little quinin, as said above, and this reaction is only sensitive 1:20,000; but the far-more sensitive tannin reaction is obtained; so that ammonia water (Reagent 1) gives the red color reaction, a not very permanent one, due to tannin, in the presence of Br. or Cl.

(a) Lime water gives a not very permanent blue violet color reaction, when added to the filtrate of the watery saturated solution of Quinin tannate.

(b) It is tested for the presence of Quinin by boiling 0.50 g. Quinin tannate with one (1) g. magnesia and fifty (50) c. c. of water; the filtrate is yellow, becomes turbid on cooling, and has an alkaline reaction to litmus paper. Acidulated with one (1) drop nitric or sulfuric acid, it becomes fluorescent and gives the thalleioquin reaction.—See *Quinin sulfate*, page 110. Tannin is not present in this filtrate, as can be proved by the negative reaction with ferric chlorid solution (Reagent 4).

The percentage of Quinin in Quinin tannate is variable.

The Dutch and French Pharmacopœia require twenty (20) per cent.

The German Pharmacopœia thirty (30) to thirty-two (32) per cent.

The British, neither the U. S. Pharmacopœia (edition 1882), contain it.

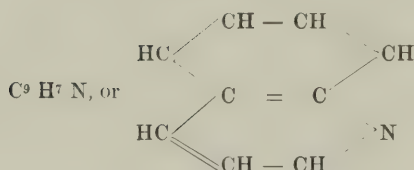
\* One (1) part of it dissolves in three (3) parts glycerol at 70° and in fifty (50) parts of one (1) per cent. hydrochloric acid (1 g. acid of 1.2 sp. gr. with 99 g. of water) at 70°.

The same Quinin tannate does only partly dissolve under the same conditions, in one (1) per cent. Sulfuric acid (1 g. acid of 1.8 sp. gr. and 99 g. of water) at 70°, in five (5) per cent. and in ten (10) per cent. acid.

The Quinin tannate was made according to the Austrian Pharmacopœia VII. in our Laboratory. Quinin tannate of German manufacture behaved the same. Compare a report in the Proceed. of the A. P. A., Vol. 32, 1884, page 309, where it was considered to be clearly proven that tasteless Quinin tannate, as a medicine is practically inert, because of its insolubility in very dilute acid (gastric juice.)

Compare also H. Beber in Ph. Weekblad for Holland, June 24, 1893.—[J. B. N.]



**Quinolin.**

Is a mobile, colorless fluid with an odor suggestive of nitrobenzol. Sp. gr. 1.094. Boiling point  $238^{\circ}$ ; its vapors are inflammable. Browns when exposed to daylight. Very little soluble in water, which solution has a pungent, hot taste, suggestive of oil of peppermint, and has no reaction to litmus paper; miscible in all proportions with ether, alcohol, amyl alcohol and chloroform; not unlimited with carbon disulfid, which may be due to the water it contains. Acids, as hydrochloric or sulfuric, become heated when mixed with Quinolin, but no neutralization takes place; no white clouds form by mixing with hydrochloric acid.

(a) Quinolin partly reduces calomel—colors it gray.

(b) The respective hydroxides of alum-, copper-, magnesium-, and zinc-sulfate are precipitated from their solution by an excess of Quinolin; from the three latter salts they dissolve partially in an excess of Quinolin. The filtrate of the magnesium sulfate mixture is alkaline; the three other salts give filtrates that are acid to litmus paper. Quinolin in excess fully precipitates the hydroxid from a ferric chlorid solution; the filtrate is acid.

(c) Quinolin redissolves the precipitate caused by it in a  $\frac{N}{10}$  silver nitrate solution, whereby the liquid remains neutral.

(d) Reagents 2, 6, 7, and 12, form white crystalline precipitates in a watery solution of Quinolin, which are colored yellow by hydrochloric acid (Reagent 5). The precipitates from Reagents 13 and 14 are not as distinctly crystalline. Reagent 11 gives a voluminous crystalline precipitate, easily soluble in hydrochloric acid (Reagent 5). Reagent 19 gives a greenish, amorphous precipitate, only after the addition of hydrochloric acid (Reagent 5). Reagent 16 gives a crystalline precipitate. Reagent 17 gives no precipitate. Reagent 24 gives a voluminous precipitate in a watery Quinolin solution.

**Quinolin Tartrate.**

3 Molecule Q., 4 Mol. Ta.

A crystalline powder of very little odor, with the taste of quinolin. Melts easily, but not at water bath temperature; chars when heated higher; whereby it gives off the peculiar odor of burning tartaric acid—somewhat similar odor to that of burning sugar. Is soluble in about eighty (80) parts water at the normal temperature; less soluble in alcohol of 94 per cent; insoluble in ether, chloroform and carbon disulfid. A solution of one part to three hundred and fifty-eight (358) parts of water, has an acid reaction to blue litmus paper. Reagents act on Quinolin tartrate as described under *Quinolin*, with the following exceptions:

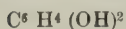
(a) Reagent 11 does not give a precipitate in a solution of the salt; crystals form in abundance, after the addition of hydrochloric acid (Reagent 5).

(b) Reagent 19 does not visibly change the solution of the salt; it colors red after the addition of hydrochloric acid (Reagent 5), and an abundant red, crystalline, precipitate forms, partly consisting of rhomboids.

(c) Gives no color reactions with nitric, or with sulfuric (Reagents 15 and 21) acids.

(d) Other Quinolin salts act like the tartrate. Reagents 11 and 19 give the above named crystalline precipitate in a mixture of an equal volume of Quinolin and of hydrochloric acid.

(e) Ammonia water (Reagent 1) and a ten (10) per cent. solution of ammonium carbonate, cause an opalescence in saturated, watery Quinolin salt solutions, which opalescence disappears on adding an excess of Reagent (1).

**Resorcinol.**

## METADIOXIBENZOL.

Forms colorless prisms or needles, according to the dissolving medium used. Melts at  $110^\circ$ ; sublimes unaltered; distills at  $276^\circ$ ; evaporates with the vapors of water. Resorcinol colors yellow brown, or reddish-pink, when exposed to daylight; has an odor suggestive of a benzoic salt and urine. Soluble in water, 10:11,5 parts at  $0^\circ$ , 10:6,8 parts of water at  $12.5^\circ$ , which solutions have a sweetish taste, with a biting after-taste. Also easily soluble in ether and in alcohol; hardly so in benzene, chloroform or carbon disulfid. Reddens moist blue litmus paper.

(a) Resorcinol dissolves in lime water (Reagent 10) with a faint lilac color, which changes to a yellow green. It dissolves in a caustic soda solution with a lilac color, which turns green or red if chloral hydrate or chloroform is added, which latter color brightens by warming to  $50^\circ$ ; it fades on addition of acids.

(b) Neither a crystal of ferrous sulfate, nor a ten (10) per cent. solution of lead subacetate has any effect upon a watery solution of Resorcinol—difference from Pyrogallol “(d)”, page 104; a ten (10) per cent. solution of lead acetate gives a precipitate, however.

(c) When dissolved in chlorin water (Reagent 3) it colors the latter brown—very temporarily lilac; the solution turns bright red when ammonia water (Reagent 1) is added.

(d) Resorcinol colors bromin water (Reagent 2) lilac—this color disappears immediately; the solution discolors, and a flocculent precipitate of tribromresorcinol is thrown down,  $\text{C}^6\text{HBr}^3(\text{OH})^4$ .

(e) Soluble in nitric acid (Reagent 15) with a red color, soon turning brown.

Resorcinol is soluble in sulfuric acid (Reagent 21) with a yellow color; a violet color reaction is obtained with sulfuric acid when a trace of nitric acid (Reagent 15) has previously been added to it. A trace of sodium nitrate ( $\text{NaNO}^3$ ) added to the sulfuric acid (Reagent 21) gives a greenish color reaction, turning brown and violet. Resorcinol gives a bright blue color reaction, if strewn upon sulfuric acid (Reagent 21) in which sodium nitrite ( $\text{NaNO}^2$ ) has been dissolved; (0.030) g. of the salt in two (2) c. c. of the acid.

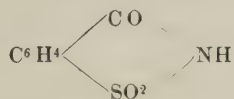
(g) A dark violet color reaction is obtained by adding a drop of ferric chlorid solution (Reagent 4) to a watery Resorcinal solution.

(h) An intense carmine-red fluid is obtained by warming carefully over the flame a mixture of 0.050 g. Resorcinol with 0.10 g. tartaric acid and ten (10) drops sulfuric acid (Reagent 21); the mixture becomes blue when oxalic acid is substituted for the tartaric; the color of the blue compound changes to an orange-red, which fades by diluting with ten (10) c. c. of water. The fluid shows dichroism by saturating with strong ammonia water, is red by transparent, green by reflected, light. One obtains a red fluid with bluish-green fluorescent properties if citric instead of oxalic or tartaric acid has been used. Succinic acid, taken instead of citric, oxalic or tartaric, produces a green fluorescence; (fluorescein reactions.)

A hot mixture of 0.010 g. sodium nitrite ( $\text{NaNO}_2$ ), one (1) c. c. of Reagent 13 or 14 and two (2) c. c. water becomes white and turbid, when 0.005 g. Resorcinol is added to it. The mixture colors dark brown, and the precipitate increases, when the warming is continued.

Resorcinol reduces silver from a  $\frac{N}{10}$  silver solution, made alkaline by ammonia water (Reagent 1).

### Saccharin.



PARTLY ANHYDRO-ORTHO-SULFAMINBENZOIC ACID  
(60 TO 70 PER CENT.)

Contains *para*- and *meta*-sulfaminbenzoic acid (30 to 40 per cent.) A bulky, whitish powder with an odor faintly suggestive of nitrobenzol which becomes stronger on warming. Melts at  $206^\circ$ , and recrystallizes when allowed to cool; it browns if heated higher, and gives off white vapors of a sweet taste and an acid reaction to blue litmus paper. It leaves no residue, if ignited on platinum foil. It is soluble in 25 to 30 parts of boiling water, from which

solution it crystallizes in rhomboids, if allowed to cool slowly; about 1:300 part of the saccharin remains in solution ( $15^{\circ}$ ). This saturated solution has an acid reaction to blue litmus paper and to methyl orange solution (1:1000)—not to a tropaölin solution. Barium nitrate solution, five (5) per cent., does not give a precipitate in it. The saturated aqueous solution tastes sweet, when diluted two hundred (200) times (pure orthosulfaminbenzoic acid is 500 times sweeter than sugar). Sulfur is precipitated if the solution is mixed with equal parts of a ten (10) per cent. sodium thiosulfate solution. Ferric chlorid solution (Reagent 4) does not act upon it.

Saccharin is soluble in alcohol 1:30, in which solution ferric chlorid solution (Reagent 4) gives no color reaction; it is less soluble in ether; much less so in chloroform, benzene and carbon disulfid; is easily soluble in ammonia water (Reagent 1) and caustic potash and soda solutions, from which it is precipitated by the addition of acids; in the potash solution it does not reduce alkaline copper tartrate solution. Sulfobenzoic ammonia is formed by the solution in ammonia water, which can be obtained in crystals by evaporation. Ferric chlorid solution (Reagent 4) gives in a solution of these crystals, which have an acid reaction, an amorphous pale red precipitate of sulfo-benzoate of iron; alcohol dissolves this with a brown-red color.

(a) Saccharin dissolves colorless in nitric or sulfuric acid (Reagents 15 and 21) even by warming on the water bath.

(b) A similar fluorescent reaction, as described under “(h)”, article *Resorcinol* (page 116) is obtained as an identity reaction of Saccharin as follows:

0.005 g. Saccharin, 0.005 g. resorcinol and three (3) drops of sulfuric acid (Reagent 21), are heated in a test tube over the flame until white vapors appear,—color reactions from yellow to red, and afterwards olive-green are seen; cool; dilute with ten (10) c. c. of water; the fluid now has dichroistic properties; is yellow by transmitted light; green by reflected light; which becomes very prominent, when saturated with a ten (10) per cent. Na OH solution, so that it is pink by transmitted, and brilliant green by reflected, light.

(c) One (1) c. c. of a freshly prepared five (5) per cent. potassium ferricyanid solution, added to ten (10) c. c. of a saturated



watery Saccharin solution (the larger quantity is preferable to the smaller because potassium ferricyanid solution is itself slightly yellowish-green), and boiled, gives a dark grass-green colored fluid.

(d) A mixture of 0.10 g. Saccharin and 0.50 g. calcium carbonate, heated in a glass tube, gives off acid vapors and an odor of bitter almond oil.

(e) Ammonia is liberated if slacked lime is substituted for the calcium carbonate.

(f) Sulfuric acid is to be detected as an oxidation product from the sulfur present in the Saccharin, by the following reaction: 0.10 g. Saccharine, and 0.50 g. Sodium carbonate, are ignited in a porcelain crucible, until the mixture chars; wash the coal with two (2) c. c. of water; filter; a five (5) per cent. barium nitrate solution gives a precipitate in the filtrate, when acidulated with nitric acid (Reagent 15), that is insoluble in strong nitric acid.

(g) Sulfur is also to be detected by melting a few milligrams of Saccharin and sodium carbonate on charcoal; nitro-prussid-sodium solution gives an intense violet color in the watery filtrate of the mass, and lead subacetate solution produces a black color.—Or, by melting a trace of Saccharin on a soda bead before the blow pipe, and by dissolving the bead in a very dilute nitro-prussid-sodium solution:—Or, by heating in a glass tube a mixture of water-free sodium acetate and Saccharin (two parts dry sodium acetate and one part Saccharin); 0.20 g. of this mixture gives off vapors, which produce a black spot on paper moistened with lead acetate solution. The reaction of sulfur and nitro-prussid-sodium can also be produced, if a piece of paper saturated with nitro-prussid-sodium solution is held in the tube over the melting mixture. Barium nitrate ( $\text{NaNO}_3$ ) gives, as before, in the solution of the melted mass in the glass tube, a sulfuric acid reaction.

(h) 0.10 g. Saccharin and 0.050 g. powdered magnesium liberates hydrogen when five (5) c. c. of water are added to the mixture; an alkaline filtrate is obtained if this mixture is repeatedly evaporated to dryness, moistened again so long as hydrogen develops, and re-evaporated. Saccharin is separated, when the mixture is stirred with a glass rod moistened with a drop of nitric acid. Sulfuric acid can be detected by the usual methods, and the reaction with ferric chlorid (page 118) is also obtained. Zinc dust can be substituted for the powdered magnesium; the filtrate is acid in this modification.

(i) Salicylic acid is a product of the melting of Saccharin (0.10 g.) with caustic soda (0.50 g.), in a silver dish. When the brown mass is dissolved in two (2) c. c. of water, and acidulated with hydrochloric acid (Reagent 5), a violet color reaction takes place, upon addition of a drop of ferric chlorid solution (Reagent 4). Chloroform or ether will extract the salicylic acid.

(j) Phenol is produced by heating Saccharin with slacked lime; drops of phenol appear when 0.10 g. Saccharin is heated with 0.50 g. of powdered slacked lime. Transfer these drops of phenol with a glass rod into one (1) c. c. of sulfuric acid, to which 0.001 g. of potassium chlorate ( $\text{ClO}_3\text{K}$ ) has been previously added; add one (1) c. c. of chloroform and shake the mixture; the under layer will have a green color.

### Salicin.

$\text{C}^{13} \text{H}^{18} \text{O}^7$

A crystalline powder of silky lustre, melting at  $210^\circ$ —the melted mass recrystallizes if allowed to cool; colors brown if heated higher, gives off vapors acid to blue litmus paper, and does not recrystallize any more; it chars at last, and develops thereby an odor suggestive of caramel.

Soluble in water at  $100^\circ$ , 1:1; at  $15^\circ$ , 1:28. It is bitter, which taste is detected in 1:3000 watery dilutions. Salicin is also soluble in alcohol of 94 per cent; in ten (10) per cent. caustic potash and soda solutions; in glacial acetic acid; very sparingly soluble in ether; insoluble in chloroform and carbon disulfid.\*

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\* The statement is incorrect that Salicin is insoluble in ether. Little discrepancies of this kind account for many differences in analytical work. Twenty-five (25) g. ether, washed free from alcohol and dried afterwards over potassium carbonate, dissolves, in the course of a day, enough Salicin to prove its presence by reactions "(a)" and "(f)". The chloroform of the U. S. P., containing one (1) per cent alcohol, does not dissolve, in the same proportion as described for ether, even a trace of Salicin. Sulfuric acid (Reagent 21) remains colorless, when added to the dish, wherein twenty-five (25) g. chloroform U. S. P. have been evaporated, which has been in contact for twenty-four hours with Salicin. A faint trace, which does not warrant an assertion that Salicin is soluble in carbon disulfid, is dissolved in twenty-five (25) g. carbon disulfid in the course of twenty-four hours, giving only a suggestion of a color reaction when treated with  $\text{H}^2 \text{SO}^4$ .—[J. B. N.]

(a) A particle of Salicin, strewn upon a few drops of sulfuric acid (Reagent 21) colors blood-red immediately; the acid remains colorless; slowly the Salicin dissolves in the acid and colors this red.

(b) Salicin dissolves colorless and easily in cold hydrochloric acid (Reagent 5); this solution deposits a voluminous, lumpy, white precipitate of *Saliretin* by warming, long before it boils.

(c) Salicin is soluble in an alkaline copper tartrate solution (Fehling's fluid), but decomposes it in a few hours, and separates red cuprous oxid when warmed on the water bath; this decomposition appears immediately at 100°.

(d) Ferric chlorid solution (Reagent 4) shows the presence of salicylic acid as a decomposition product, when 0.050 g. Salicin is heated in a glass tube until it browns, and the residue when cool, washed with two (2) c. c. of water. One drop of the ferric chlorid solution gives a violet color to the watery fluid.

(e) A ten (10) per cent basic lead acetate solution precipitates Salicin as salicinate of lead, from a saturated, watery solution (15°).

(f) A few particles of salicin, strewn upon a freshly prepared mixture of 0.020 g. ammonium molybdate in five (5) drops of sulfuric acid, becomes purple colored immediately.

(g) The aromatic odor of salicylaldehyd  $C^6H^4(OH)CHO$ , is developed by warming 0.050 g. of Salicin, dissolved in two (2) c. c. of Reagent 17, with five (5) drops of sulfuric acid (Reagent 21), until it commences to color brown.

(h) A yellow colored fluid is obtained when the solution of 0.050 g. Salicin in three (3) c. c. of nitric acid is evaporated to dryness on the water bath, and the residue redissolved in two (2) c. c. of water. Ferric chlorid solution (Reagent 4) gives a red color reaction now, if this yellow fluid is evaporated to dryness and the residue redissolved in one (1) c. c. of water;—this red color reaction is due to nitro-salicylic acid. Salicylic acid and salol (see pages 126) behave the same.

**Salicylic Acid.**

## ORTHOXYBENZOIC ACID.

Needles or prisms, according to whether it is crystallized from a watery or from an alcoholic solution. Melting point  $156^{\circ}$ , recrystallizing when allowed to cool; is partially decomposed into carbon dioxid ( $\text{CO}^2$ ) and phenol ( $\text{C}^6\text{H}^5\text{OH}$ ), when heated higher; some Salicylic acid remains undecomposed, when 0.030 g. is mixed and ignited with 1.50 g. slacked lime. One (1) drop of the ferric chlorid solution (Reagent 4) gives a violet color reaction on Salicylic acid when the residue of the ignition is exhausted with five (5) c. c. of water, and one (1) drop of hydrochloric acid (Reagent 5) added to the filtrate; more of the Reagent produces a brown color; an excess of alkali has also an influence on the color, prevents frequently the color reaction entirely.

Salicylic acid has a very slightly acid and acid taste, with a not disagreeable sweet after-taste; it scarcely affects the throat, but is purgent to the nasal membrane, inducing sneezing. Is soluble 1:13 in water at  $100^{\circ}$ , 1:444 at  $15^{\circ}$ , 1:1000 at  $0^{\circ}$ . A watery solution of 1:500 has an acid reaction to litmus, an agreeable taste, and becomes permanently violet colored on addition of one (1) drop of Reagent 4. Salicylic acid is as sensitive to ferric salts as potassium sulfocyanate is.\* It requires only more time, in large dilutions, while a few drops of a ten (10) per cent. potassium sulfocyanate solution reacts upon ferric salts in an acidulated solution *immediately*; it is sensitive in a 1:500,000 dilution, watery or alcoholic,—difference as compared with phenol, which does *not* give a violet color reaction with ferric salts in an alcoholic solution.—Compare “(a)”, article *Phenol*.

A method for the determination of Salicylic acid and phenol together, based on this difference, is given in the *Chem. Zeitung* No. 5, 1893, page 69, by Dr. A. Fajans.

The acid in its crystalline state also colors the ferric chlorid

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\* The red color must not disappear by warming;—distinction from NO, that also gives a blood-red color with a rhodanate, disappearing, however on warming.—[J. B. N.]



solution. A more reddish color is obtained from neutral salicylates, which color changes to violet, however, on acidulating the fluid with dilute hydrochloric or sulfuric acid.

It is very soluble in ether and in alcohol; also easily soluble in acetone, amyl—and methyl alcohol, glycerol, and chloroform; sparingly soluble in carbon disulfid.

(a) It dissolves in cold sulfuric acid (Reagent 21) colorless (if slightly colored, impurities are present); the acid becomes brown colored, when boiled with it.

(b) No color reaction takes place when one (1) c. c. sulfuric acid (Reagent 21) is poured over a mixture of 0.050 g. Salicylic acid and 0.010 g. sodium nitrate ( $\text{Na NO}_3$ ); the fluid reddens, however, in the course of three hours, when sodium *nitrite* ( $\text{Na NO}_2$ ) has been substituted for the nitrate.

(c) It dissolves in cold nitric acid (Reagent 15) also nearly colorless; with a red color, however, on slightly warming. This solution turns pale yellow when boiled; yellow needles of nitro-salicylic acid form in it by cooling, which are soluble in ammonia water (Reagent 1) with a red color. The watery solution of nitro-salicylic acid, is colored red by an addition of Reagent 4; not violet.—Compare *Methacetin*, page 73; *Phenacetin*, page 91; *Salicin*, page 120, and *Salipyrin*, page 124, reactions.

(d) 0.160 g. Salicylic acid and 0.110 g. Borax, dissolved by slightly warming in one (1) c. c. of water, forms in the cold crystals of the formula  $\text{C}^6\text{H}^4(\text{OH})\text{COO}(\text{BO}) + \text{C}^6\text{H}^4(\text{OH})\text{COONa}$ ; the mother liquor has an acid reaction to litmus paper, colors tumeric paper brown, gives a violet color reaction with Reagent 4, and has a strong bitter taste. Sodium salicylate is sweet.

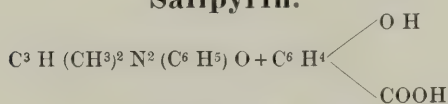
(e) The watery saturated solution of Salicylic acid gives a heavy precipitate with a lead subacetate solution; not with a neutral ten (10) per cent. lead acetate solution.

(f) The agreeable odor of wintergreen oil (*oleum gaultheriæ procumbentis*) is developed, when a previously prepared mixture of twenty-five (25) c. c. of methyl alcohol with ten (10) c. c. of sulfuric acid (Reagent 21), in which mixture 0.050 g. Salicylic acid is afterwards dissolved, is distilled. Reject the first five (5) c. c. of the distillate; cool the flask containing the mixture, and heat it for the second time, to observe the salicylate of methyl (gaultheria oil) odor.



(g) No precipitate is obtained by mixing a neutral solution of sodium salicylate with barium nitrate or calcium chlorid solution; after a while crystals of calcium salicylate form in the mixture. Neutral lead acetate solution give immediately a precipitate with sodium salicylate solutions.

### Salipyrin.



#### ANTIPYRIN SALICYLATE.

A colorless, crystalline powder, possessing the sweetish, acrid taste of salicylic acid. Melting point  $92^\circ$ , charring when heated higher, whereby it gives off vapors of an acid reaction. Soluble 1:25 in water at  $100^\circ$ , 1:200 at  $15^\circ$ . The solutions have an acid reaction to litmus paper and likewise to methyl orange solution, 1:1000—not to tropaölin; they decompose a normal thiosulfate solution. It is very soluble in chloroform; less so in ether, and in alcohol of 94 per cent.; sparingly in carbon disulfid.

(a) A ten (10) per cent. lead subacetate solution gives a voluminous precipitate in a saturated watery solution of Salipyrin ( $15^\circ$ ). —A ten (10) per cent. lead acetate solution does not give a precipitate.

(b) Chlorin water (Reagent 3) causes a turbidity in its watery solution (liberation of salicylic acid).

(c) Reagents 2, 6, 7, 12, 13, 16 and 24 give precipitates in its saturated watery solution; Reagent 17 does not.

(d) Crystalline tufts are formed and sink to the bottom if one (1) c. c. of Reagent 16 is added to ten (10) c. c. of the watery Salipyrin solution.

(e) Salicylic acid is liberated in crystals when 0.20 g. Salipyrin is dissolved by warming in two (2) c. c. of water and four (4) c. c. of hydrochloric acid (Reagent 5), and the fluid allowed to cool.

(f) On cold nitric or sulfuric acid (Reagents 15 or 21), Salipyrin has no effect; it becomes a little brown colored, when boiled with Reagent 21.

(g) Salipyrin differs from antipyrin and from salicylic acid in that it gives a dark, fiery-red fluid, changing to violet and blue, when warmed with nitric acid (Reagent 15); a black, greasy matter forms thereby in the fluid.

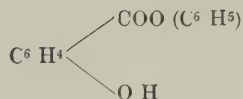
(h) A bluish-green fluid, fading to yellow, is obtained, when ten (10) drops of acetic acid are mixed with ten (10) c. c. of a saturated (15°) watery solution of Salipyrin, to which 0.10 g. sodium nitrite ( $\text{Na NO}_2$ ) has previously been added.

(i) A bluish-green mixture is obtained, which colors red, and in which small crystals of nitroso-antipyrin form,—compare *Antipyrin*, “(h)”, page 10,—when 0.10 g. Salipyrin, 0.10 g. sodium nitrite ( $\text{Na NO}_2$ ) and 0.20 g. mercuric chloride ( $\text{HgCl}_2$ ) are agitated together under addition of four (4) c. c. of water.

(j) The residue of sodium salicylate, obtained from 0.50 g. Salipyrin when evaporated and dried on the water bath with one (1) c. c. of a ten (10) per cent. caustic soda solution and four (4) c. c. of alcohol of 94 per cent., must be neutral or of an alkaline reaction. Chloroform (57 per cent. of the amount of Salipyrin) dissolves antipyrin from this residue by warming; this chloroform solution must, moreover, leave by spontaneous evaporation a crystalline mass which gives a clear, red (not a violet) colored solution when boiled with a few c. c. of nitric acid (Reagent 15).

(k) One (1) drop of Reagent 4, added to one (1) c. c. of a saturated, watery (15°) solution of Salipyrin, diluted with nine (9) c. c. of water, gives a reddish violet colored fluid. The mixture is yellow-brown when diluted to one hundred (100) c. c.; it fades to a pale yellow fluid when one hundred (100) c. c. more of water are added, and the solution is soon covered with a layer of yellowish-brown flakes of antipyrin—compare *Antipyrin*, page 11, “(k)”; these antipyrin flakes dissolve on the addition of two (2) drops of hydrochloric acid (Reagent 5), whereby the solution takes a lilac color; this same color reaction appears when the Salipyrin solution has previously (instead of afterwards) been mixed with one (1) drop of hydrochloric acid (Reagent 5), one (1) drop of Reagent 4, and diluted with two hundred (200) c. c. of water. These color reactions are plainer when the solution is less dilute.

(l) A brown mixture is obtained from the mixture of one (1) c. c. of the Salipyrin solution with two (2) c. c. of Reagent 4. An addition of more Salipyrin solution changes the color to violet.

**Salol.**

## PHENYLSALICYLATE.

A white crystalline powder of an agreeable, faint, aromatic odor, suggestive of methylsalicylate, and a sweet taste; it feels gritty between the teeth. It melts at  $42.5^{\circ}$ , when previously dried over  $\text{H}^2\text{SO}^4$ —gives off a pleasant odor and remains in the fluid state at  $15^{\circ}$ , for a few hours, before it solidifies again; when heated higher it gives off vapors of a peculiar odor and faintly acid reaction; it partly chars, and phenol is liberated, which can be extracted with water. Reagent 4, added to the filtrate, colors it violet. Salol dissolves largely in ether, alcohol, chloroform and benzene.

(a) It is nearly insoluble in water at  $100^{\circ}$ ; the fluid becomes turbid, however, when allowed to cool; Reagent 4 colors the filtrate violet.

(b) 0.005 g. Salol dissolves with a yellow color in five (5) drops of sulfuric acid (Reagent 21) on warming; the color increases in intensity to a pale red, when heated nearly to the boiling point. One drop of Reagent 4 colors this solution violet, after it has been diluted with ten (10) c. c. of water; an agreeable odor develops, when this watery dilution is boiled. But if one (1) drop of Reagent 4 is added to the solution of 0.05 g. Salol in one (1) c. c. of the acid, a dirty green fluid, which soon becomes turbid, is obtained.

(c) Salol gives no reaction with nitric acid (Reagent 15). But if a solution of 0.050 g. Salol in three (3) c. c. of nitric acid is evaporated to dryness, it yields a brown-yellow colored fluid, when the residue of the evaporation is treated with ammonia water (Reagent 1). Water hardly dissolves it.—Compare similar reaction with *Salicin*, page 121. Reagent 4 colors the fluid red, when the excess of ammonia has been expelled.

(d) It dissolves in Reagent 22 with a yellow color reaction.

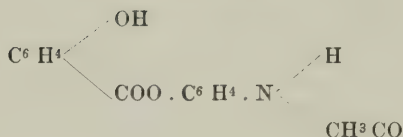
(e) In its crystalline state it does not act upon Reagent 4. 0.050 g. Salol, triturated with a glass rod of the size of a match, moistened at the point with a trace of Reagent 4, shows no reac-

tion, not even after the addition of one-half (0.5) c. c. of water. The mixture colors violet, however, when five (5) c. c. of alcohol is added. One (1) drop of Reagent 4 increases the color; a larger addition of the same Reagent changes the violet color to brown.

(f) A drop of Reagent 4 gives a violet color reaction, in a mixture of three (3) c. c. of Ammonia water (Reagent 1), warmed in a loosely corked flask with 0.010 g. Salol, and after two hours evaporated down to one (1) c. c. The ammonia water becomes brown colored, if left in contact with Salol for a few days.

(g) A solid mass is obtained when 0.20 g. Salol, rubbed to a fine powder, is mixed with one (1) c. c. of a ten (10) per cent. caustic soda solution; slight warming facilitates the action; Salol dissolves clear in the soda solution, when the warmth is increased, and often it becomes red-colored thereby; the same red color appears when hydrochloric acid (Reagent 5) is added to the mixture; salicylic acid precipitates in red-colored crystals. Phenol is liberated and can be detected by its odor, as well as by adding ammonia water (Reagent 1) in excess to the filtrate of salicylic acid, and by mixing it with an equal volume of bromin water (Reagent 2). The fluid colors greenish-blue when the bromin vapors evaporate, and chloroform becomes red-colored when agitated with it.

(h) A bright greenish-blue solution is obtained when one (1) c. c. of sulfuric acid (Reagent 21) is added to a mixture of 0.050 g. Salol and 0.080 g. sodium nitrate ( $\text{Na NO}_3$ ). The mixture is *red* at first, changing to brown, and then to a bluish rather than a green color, when sodium *nitrite* ( $\text{Na NO}_2$ ) is substituted for the nitrate. These color reactions go over into red, and fade, when the sulfuric acid attracts moisture or when it is diluted with water.

**Salophen.**

ACETYL-PARAAMIDOPHENOL. ACETYLPARAAMIDOPHENOL SALICYLIC-ESTER.

Crystalline scales, melting at  $188^{\circ}$ , evolving vapors of a sweetish aromatic odor and of an acid reaction to litmus when heated higher. They are readily soluble in chloroform; less so in ether or alcohol; insoluble in carbon disulfid.

(a) A filtrate containing salicylic acid is obtained when 0.10 g. Salophen is charred, the residue warmed with one (1) c. c. of water, and filtered off. One (1) drop of ferric chlorid solution (Reagent 4) produces a violet color reaction in said filtrate.

(b) Reagents 15 and 21 do not alter Salophen, in the cold.

(c) A filtrate of Salophen that has been boiled with water, deposits on cooling but very few small crystals.

(d) A mixture of 0.10 g. of Salophen, 0.10 g. of chloral hydrate, and of one (1) c. c. of a ten (10) per cent. caustic soda solution, becomes of a blue or greenish-blue color, gradually turning brown or black; the same reaction will be obtained by using one (1) c. c. of chloroform instead of 0.10 g. of chloral hydrate; and a somewhat similar color reaction is obtained in a mixture of Salophen, sulfuric acid (Reagent 21) and sodium nitrite ( $\text{Na NO}^2$ ).—Compare *Salol*, “(h)”, page 126.

Salophen splits up into salicylic acid (51 per cent.) and Acetylparaamidophenol, by boiling it with caustic potash.



**Santonin.**

Santonin forms rhombic prisms, or shining plates, of a bitter taste. Melts at  $170^{\circ}$  to a colorless fluid, solidifying to a crystalline mass—if carefully heated, however, it sublimes unaltered; it gives off white vapors when heated higher than its melting point; the fluid becomes reddish brown, and solidifies to a brown, clear, glass-like mass; a red color is made prominent when a little dry KOH, Na OH, or  $\text{Ca}(\text{OH})^2$  has been added. Heated on platinum foil it burns with considerable smoke.

Soluble 1:4 in chloroform; 1:40 in alcohol of 0.83 sp. gr., which solution is very bitter; 1:160 in ether; 1:5000 in water, at  $15^{\circ}$ ; soluble 1:250 at  $100^{\circ}$ , which solution is hardly bitter to writer when cooled, five (5) c. c. of it being taken for this test. It is also easily soluble in strong acetic acid [eighty (80) per cent.] and slightly so, four (4) per cent., in olive oil by warming ( $50^{\circ}$ ). Santonin has no reaction upon litmus paper. Is colored yellow on exposure to light. The yellow crystals dissolve in chloroform or in alcohol of 0.83 sp. gr., with a pale-yellow or lemon color, but recrystallize colorless; they dissolve with a yellow-red color in an alcoholic solution of potassa or of ammonia.

Santonin affects the eyesight when taken internally, in large doses (0.20 g.)—causing so-called xanthopsia, when all white objects appear yellow, and blue objects green.

(a) 0.005 g. Santonin, agitated with five (5) c. c. of a ten (10) per cent. alcohol caustic potash or soda solution, give a bright-carmine-red colored fluid, which fades slowly.—Compare “(e)”.

(b) Santonin (0.010 g.) dissolves clear in one (1) c. c. sulfuric acid (Reagent 21), subsequently very slowly taking a yellow color—it sometimes takes a day; a reddish and brown color succeeds the yellow in the course of an hour *if* the mixture is frequently agitated; if a small lump of Santonin is taken, *this* turns red. Iso-santonin is precipitated from this acid solution, after it has been kept for a few hours on the water bath and diluted with water. Iso-santonin has the same composition as Santonin, melts at  $138^{\circ}$  after being washed and recrystallized from boiling alcohol of ninety-four (94) per cent., and does not color yellow, when ex-

posed to the light.—Iso-santonin remains colorless when warmed with sulfuric or phosphoric acid.

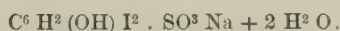
(c) 0.010 g. Santonin, evaporated on the water bath with one (1) c. c. of dilute phosphoric acid of 1.154 sp. gr. gives the same reaction as with sulfuric acid just mentioned “(b)”, but the colors are far brighter, the red more of a purple tinge, and the reaction takes place quicker.

(d) 0.005 g. Santonin warmed on the water bath with two (2) c. c. of sulfuric acid of 1.56 sp. gr. [obtained by mixing two (2) c. c. of sulfuric acid of 1.84 sp. gr. with one (1) c. c. of water and cooling the mixture], gives a colorless solution, which turns faintly yellow, *very slowly*; it becomes violet colored when stirred with a glass rod of the size of a match, previously moistened with a trace of Reagent 4. Dilution with alcohol or water does not alter the color. Neither ether or chloroform extract the color from the solution.

This same reaction does not take place as well, when 0.005 g. Santonin is agitated with two (2) c. c. of sulfuric acid of 1.84 sp. gr. and one (1) c. c. of water, and one (1) drop of Reagent 4 is stirred into the hot mixture.

(e) Another characteristic purple-red color reaction—compare “(a)” —is obtained when a mixture of one (1) g. of slacked lime and one (1) g. of sodium carbonate is moistened with two (2) c. c. of alcohol of 94 per cent., and 0.005 g. Santonin stirred in; the mixture has to be slightly warmed, for this reaction; the color is not permanent.

(f) Santonin, thrown upon a drop of Reagent 22, gives no reaction; the reagent colors green only in course of an hour. But this is no distinctive reaction for Santonin.

**Sozo-Iodol Sodium.****DIIODOPARAPHENOLSULFONIC SODIUM.\***

Forms colorless and nearly odorless fine needle-like crystals of a salty taste, suggestive of potassium iodid, and with a decidedly sweetish after-taste, that can be detected in a 1:200 dilution. It is soluble in water, 1:15 at 15°; very soluble in alcohol; less so in chloroform; hardly at all in ether or carbon disulfid. When a watery solution is exposed to direct sunlight for a few hours, iodin is liberated—much sooner liberated when either the dry or moist salt is heated. A watery solution cannot be warmed on a water bath without decomposition.

(a) A few drops of bromin water (Reagent 2), or of chlorin water (Reagent 3), and also one (1) drop of a ferric chlorid solution (Reagent 4), added to five (5) c. c. of a watery solution (1:100) of the salt, to which previously one (1) drop of a freshly gelatinized starch solution has been added, gives immediately the iodin reaction on starch.

A drop of nitric acid (Reagent 15) added to a few particles of the salt, colors the latter dark-brown, owing to liberated iodin, the presence of which can be proved by adding one (1) c. c. of water and one (1) drop of the very dilute freshly gelatinized starch solution to the mixture.

Sulfuric acid (Reagent 21) does not act upon Sozo-iodol sodium.

(b) Sozo-iodol sodium gives a charcoal which ignites with difficulty, when heated in an open crucible, owing to the formation of sodium sulfate and carbonate. A five (5) per cent. barium nitrate solution gives a precipitate in the acidulated (nitric acid) filtrate of the residue of the ignition.

(c) Sozo-iodol sodium has an acid reaction in a watery solution of 1:100 on litmus paper; on methyl orange, 1:1000; on lacmoid 1:500; not on tropaolin.

(d) A small drop of Reagent 4 gives in fifty (50) c. c. of a watery solution (1:100) of Sozo-iodol sodium, a strong, violet color reaction.

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\* Compare Amer. Jour. of Pharm. 1888, pages 239, 621; 1889, page 17; 1890, page 384.

(e) The watery solution (1:100) soon becomes brown from liberated iodine, if mixed with equal parts of nitric acid (Reagent 15).

(f) Neither one (1) c. c. of a five (5) per cent. barium nitrate solution, of a ten (10) per cent. lead acetate solution, nor of a  $\frac{N}{10}$  silver nitrate solution, gives a precipitate in five (5) c. c. of a 1:100 watery solution, when strongly acidulated with nitric acid (Reagent 15). The barium nitrate and lead acetate solutions give voluminous precipitates in a 1:100 watery solution, when *not* acidulated with nitric acid—in a few minutes becoming crystalline in the case of the barium nitrate, and amorphous with the lead acetate solution; the precipitate of the lead reaction is at first white, but soon becomes yellow.

$\frac{N}{10}$  silver nitrate solution gives in a watery solution 1:4000 a turbidity, which will become somewhat crystalline. The lead reaction is more sensitive, but the precipitate is amorphous.

(g) Crystals of trinitrophenol (picric acid) are obtained, when a part of Sozo-iodol sodium is evaporated with a quantity of nitric acid and the residue washed and filtered through glass wool. The yellow filtrate contains also sulfuric acid, to be detected with a barium nitrate solution.

### **Sparteïn Sulfate**



A crystalline powder. Melts in a glass tube above 220° to a clear and colorless fluid, solidifying again as crystals; heated higher, it chars.

Easily soluble in water and in alcohol, which solutions have a bitter taste; an acid reaction to litmus paper, and to a 1:1000 methyl orange solution; they dilate the pupil. Chlorine water (Reagent 3) does not act upon it, neither any mineral acid, whether pure or in combination with sodium nitrite ( $Na NO^2$ ) or ferric chlorid. It gives no color reaction with sulfo-molybdate of ammonia.

The following reactions are to be made with a watery solution of the salt 45:1,000.

(a) A precipitate is given by ammonia water (Reagent 1) in one (1) c. c. of the above prescribed solution of Sparteïn sulfate, which dissolves when about three (3) c. c. of the Reagent has been added.

(b) Reagent 6 causes a turbidity in one (1) c. c. of this dilution, turning into black crystals.

(c) Reagent 7 gives a voluminous brown precipitate in one (1) c. c. of it, which changes to a black crystalline sediment.

(d) Reagent 12 causes a crystalline precipitate in course of a few hours in one (1) c. c. of this dilution.

(e) A yellow precipitate is obtained, when four (4) c. c. of bromin water (Reagent 2) is added to one (1) c. c. of this dilution which, however, dissolves, in course of time; but the smallest addition of bromin water causes it to reappear.

(f) It is not sensitive in this dilution to Reagents 11, 13, 14 and 17.

(g) Crystals of  $C^{15} H^{26} N^2(HCl)^2 HgCl^2$  form, when 0.050 g. of the salt is dissolved in four drops of Reagent 13, to which one (1) drop of dilute hydrochloric acid (1.061 sp. gr.) and one (1) c. c. of water is added.

(h) Crystals are formed also, but slower, if 0.050 g. of the salt is dissolved in one (1) c. c. of Reagent 14 and one (1) drop of hydrochloric acid (Reagent 5) added to the turbid mixture.

(i) Voluminous, amorphous, precipitates are obtained in one (1) c. c. of a two (2) per cent. solution of the salt, by a few drops of Reagents 16 and 24.

(j) Reagents 18 and 19 give in this dilution, shining, yellow, crystalline laminae.

(k) Five [5] drops of a ten (10) per cent.  $Pt Cl^4 HCl$  solution yield, on shaking with one (1) c. c. of the solution of Sparteïn sulfate, a heavy curdling, yellow precipitate, dissolving when an additional five (5) c. c. of cold water ( $12^\circ$ ) is added.

(l) If 0.10 g. of the salt and an equal part of potassium iodate ( $KIO^3$ ) are triturated with five (5) c. c. of water, a brown-red fluid is obtained, without the liberation of iodine; but the latter is liberated immediately, when a few drops of acetic acid are added to the mixture. This is not, however, an identity reaction on Sparteïn.—Compare *Morphin*, page 77.

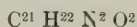
(m) A crystal of the salt, dropped into a drop of  $(NH^4S)^2 HS$  causes immediately an orange-red color reaction, that fades some-



what, but reappears permanently when the mixture is spontaneously evaporated to dryness.

(n) Sparteïn is liberated as a colorless liquid alkaloid, lighter than water, with an odor faintly suggestive of pyridin, when ten (10) drops of ten (10) per cent. caustic soda solution are agitated with 0.050 g. of the salt. It is so little volatile at the ordinary temperature, that red litmus paper remains unaffected when a piece is suspended over it in the test tube in this test; it turns blue, however, when the test tube is slightly warmed. Boiling point of Sparteïn 300°.

### Strychnin.



Strychnin crystallizes in prisms, but is usually obtained as a white, amorphous powder. Melting point 268° (268°).—Compare proceedings of the Amer. Phar. Assoc. for 1891, page 620.

It is easily soluble in chloroform, 1:16, at 15°; in alcohol of 0.833, sp. gr., 1:160, at 15°; 1:12 at the boiling point; in absolute alcohol 1:200 at 15°; in benzene 1:170, at 17°; in amyl alcohol 1:185, at 15°; in glycerol of 1.24, sp. gr. 1:300; in carbon disulfid 1:485, at 15°; in ether 1:1250, at 15°; it is also easily soluble in warm turpentine.—Compare *Brucin*, page 23.

A watery solution is intensely bitter, a bitterness that is distinctly perceptible to writer [J. B. N.] in a 1:600,000 dilution, when five (5) c. c. are swallowed.—Compare *Brucin*, page 24.

(a) Nitric acid of 1.15 sp. gr. and more dilute (1.06 sp. gr.) dissolves Strychnin and Strychnin salts with a yellow color.

(b) Neither sulfuric (Reagent 21) or hydrochloric (Reagent 5) acid gives a color reaction, in the cold; a yellow, or yellow-brown color is only to be noticed on warming.

(c) A bright blue-violet color reaction (changing in less than a minute to red when only a trace [see page 136] is present, and lasting comparatively longer with a larger quantity of the alkaloid) is obtained with Strychnin or any of its salts, is dissolved

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\* It browns a little at 210°, which brown color does not increase up to 260°, and is very little more prominent at 265°. The strychnin must be previously dried at 105°, melted in a dry capillary tube, and this tube submitted to the test inside of another tube.—[J. B. N.]

in sulfuric acid (Reagent 21), or in concentrated, so called, sirupi phosphoric acid (sp. gr. 1.7), and oxidizing agents are added, such as potassium permanganate, chromic or hydriodic acid, potassium dichromate, potassium ferrieyanid, peroxid of lead and of manganese, or cerous hydroxid.

To succeed with this reaction, dissolve a small particle of Strychnin, or of one of its salts, in one or two drops of sulfuric (Reagent 21) or of phosphoric acid, on a porcelain lid; throw a few minute particles of any of the above named oxidizing substances upon the acid, and move the lid slowly to and fro. Or, rub into the mixture with a glass rod, of the size of a match. Or, throw a particle of Strychnin or of one of its salts upon a few drops of Reagent 22. Or, dissolve a particle of Strychnin in one (1) c. c. of sulfuric acid (Reagent 21) in a narrow test tube and drop in a small particle of potassium dichromate or permanganate.

All the oxidizing agents named are, of course, not equally sensitive, and the most successful color reactions are obtained with dilute solutions or with fractions of a milligram. Potassium permanganate is the most sensitive reagent, and the drawback complained of by some authors that it, itself, with concentrated sulfuric acid, gives a cherry-red color reaction that is confusing, is due to improper proportions, or to too large a quantity for the reaction. The color reaction of  $\text{KMnO}_4$  with sulfuric acid alone, cannot be mistaken for a Strychnin reaction; the blue violet streaks of a Strychnin color reaction being very characteristic. It is preferable to employ Reagent 23, and not  $\text{KMnO}_4$  in substance.

Evaporate, to verify the reaction, one (1) c. c. of the dilutions that have been used for examining the bitterness of the alkaloid, on different porcelain lids, to dryness; dissolve the residue in one (1) drop of sulfuric acid (Reagent 21), divide this with a small glass rod over the whole surface and throw a very few fine particles of potassium permanganate into one lid, a very few fine crystals of potassium dichromate into another, a very few crystals of potassium ferrieyanid into a third, very little finely pulverized manganese dioxid (a good commercial article, containing not less than 90 per cent.  $\text{MnO}_2$ ) into a fourth, and a little cerous hydroxid in a fifth. Move the lids slowly to and fro, or rub with a glass rod of the size of a match.

As already said, potassium permanganate is the most sensitive

reagent. It detects 0.000001 g. ( $\frac{1}{1,000,000}$ ) Strychnin, the reaction being obtained with one (1) c. c. of the solution "C"—compare *Brucin*, page 24;—being a dilution of ten (10) c. c. of solution "B" to one (1) liter in this case. Use Reagent 23.

Potassium dichromate is the second best. Writer [J. B. N.] cannot detect a 0.000001 g. ( $\frac{1}{1,000,000}$ ) of Strychnin with it, as with Reagent 23; neither in the residue of evaporation of one (1) c. c. of the same dilution as above, and dry  $K^2 Cr^2 O^7$  with Sulfuric acid, nor with one (1) c. c. of said dilution and Reagent 22.\*

Potassium ferricyanid in fine crystals, is a very good reagent in large dilutions of Strychnin; so is cerous hydroxid. It is some times advantageous that the sulfuric acid used in these tests should have attracted a little moisture; the reaction takes place more slowly, but is more decisive.

By taking one (1) c. c. of a 1:500,000 dilution, which is decidedly bitter, potassium dichromate does not give any reaction on Strychnin; neither does manganese dioxid or cerous hydroxid; potassium ferricyanid shows in the residue of one (1) c. c. of 1:300,000 dilution a faint rose-colored reaction.

Cerous hydroxid has a great advantage over  $KMnO^4$  and over  $K^2Cr^2O^7$  in that it is white. Writer prepares it for Strychnin testing by dissolving cerium oxalate in ten (10) per cent. dilute sulfuric acid, precipitating with ammonia of thirty (30) per cent., filtering and washing. The moist cerous hydroxid gives a beautiful color reaction in 1:100,000 g. of Strychnin, changing to rose-red.

Brucin and morphin prevent, in peculiar proportions, the color reaction with Strychnin, potassium dichromate or permanganate and sulfuric acid.

No Strychnin reaction appears with Reagent 22, when brucin and Strychnin, mixed in equal parts, are submitted to the test; it succeeds, however, in this proportion, with Reagent 23. If the brucin is only one-tenth (0.1) of the mixture, the blue-violet color reaction is obtained. A large excess of atropin does not prevent or obscure a Strychnin reaction. A solution of 0.001 g. atropin sulfate evaporated to dryness, together with five (5) c. c. of the 1:100,000 Strychnin solution, has no influence upon the reaction; neither in the proportion of 0.001 g. to one (1) c. c. of the 1:100,000

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\* Compare Arch. d. Pharm., '92, page 551.

Strychnin solution; neither has cinchonin or quinin any effect. Morphin obscures the reaction in the following proportions:

A solution of 0.00001 g. Strychnin, evaporated with a solution of 0.001 g. morphin sulfate, on a water bath, yields a blurred, Strychnin reaction, when the residue is dissolved in Sulfuric acid (Reagent 21) and a crystal of  $\text{KMnO}_4$  added. But still there is evidence whereby to *suspect* the presence of Strychnin.

A solution of 0.002 g. morphin sulfate, treated in like manner with 0.00001 g. Strychnin, yields like results.

A solution of 0.003 g. morphin sulfate, evaporated to dryness, with a solution of 0.00001 g. Strychnin, yielded results in the  $\text{KMnO}_4$  test, the same as if no Strychnin was present.

A solution of 0.001 g. morphin sulfate, treated as above, with a solution of 0.0001 (1:10000) g. Strychnin, offered positive proof of the presence of the latter.

Brucin can be destroyed in a mixture of Strychnin and Brucin, by warming it for one-half hour with nitric acid of 1.056 sp. gr., to  $50^\circ$ .—Compare *Brucin*, “(f)”, page 23. A few drops of the fluid, when yellow, give Strychnin reactions with Reagents 22 and 23.—Or brucin and Strychnin, when both present as a result of a verification (examination) of a fluid extract, or of a tincture of *Semina Strychni* can be precipitated as picrates; and the brucin can be destroyed in the mixture of the picrates.\*

Quantitative experiments by writer [J. B. N.]:

Strychnin taken:—	Strychnin found:—
0.028	0.026
0.032	0.032
0.023	0.0225
0.034	0.0332
Brucin taken:—	Brucin found:—
0.021	None.
0.032	None.
0.016	None.
0.068	None.
Strychnin and Brucin mixed:—	Strychnin found:—
0.050 + 0.050	0.054
0.1 + 0.096	0.086

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\* *Gerock's* process. Compare *Archiv der Pharmacie*, 1889, page 158. For a critique of this process, by J. B. Nagelvoort, see *Proceedings of the Amer. Pharm. Assn.* for 1893.



Strychnin can be detected plainly with Reagent 23 in an evaporation residue of fluid extract Sem. Strychni *when very dilute*—imperfectly, with Reagent 22. Evaporate one (1) c. c. of fluid extract Sem. Strychni to dryness; add two (2) c. c. water to the residue; stir with a glass rod; filter; dilute filtrate with an equal proportion of water; divide a few drops over a large surface in evaporating dishes, or on porcelain lids; evaporate to dryness and add to one residue with a glass rod, one drop of Reagent 22, to another of Reagent 23. A blue-violet reaction, immediately disappearing, takes place; usually brucin and Strychnin are present in about equal proportions, varying somewhat.

Or add two (2) drops of the filtrate to one (1) c. c. of Reagent 23, contained in a narrow tube, and shake. The Strychnin reaction does *not* appear, when Strychnin or a Strychnin salt *dissolved in glycerol* (1:300) is used in testing with sulfuric acid containing chromic acid (Reagent 22). Reagent 23 and cerous hydroxid show the presence of Strychnin; Reagent 23 by the blue-violet color, the cerous hydroxid by a fairly permanent pink color, when it is stirred into the glycerol-strychnin solution, to which previously an equal part of sulfuric acid, Reagent 21, has been added.

### **Strychnin Nitrate.**



Ignites when heated to 140°. It is soluble in water and in alcohol of 94 per cent., 1:90, at 15°. A saturated, watery solution of the salt does not act upon litmus.

(a) Reagents 6, 12, 13, 14, 16, 17, 18 and 24 give precipitates with it. The precipitate caused by Reagent 24 is soluble in an excess thereof. The precipitate from Reagent 17 is crystalline; dissolved in sulfuric acid, it gives the blue-violet characteristic Strychnin reaction; the same can be said regarding the precipitate obtained by Reagent 16; it gives a Strychnin reaction, when a solution of it is brought in contact with Reagent 22.—Compare Flückiger, Pharm. Chemie, II., page 517.

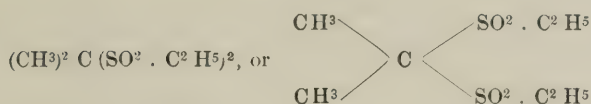
(b) A red colored fluid is obtained when Strychnin nitrate or a



saturated watery solution of the salt is boiled with hydrochloric acid.

(c) The presence of nitric acid cannot very well be verified in the salt by the usual analytical method, with a crystal of ferrous sulfate, and sulfuric acid. Diphenylamin is a better reagent; —0.010 g. of diphenylamin is triturated in a dish with a few drops of water, and five (5) c. c. of sulfuric acid (Reagent 21) added to the mixture. A dark blue, fairly permanent color reaction is obtained if one (1) drop of a saturated watery solution of the salt is carefully laid upon the surface of the acid.

### Sulfonal.



DIMETHYLMETHANDIETHYLSULFON. — DISULFONETHYLDIMETHYLMETHAN.—DIETHYLSULFONDIMETHYLMETHAN.

A colorless (white) crystal powder. Melting point 126°, when it becomes a colorless fluid, recrystallizing on being allowed to cool; when this fluid is heated in a glass tube it gives off white vapors of an acid reaction to litmus paper and of the odor of sulfurous acid; heated further, it chars.

Is soluble in water, 1:500, at the normal temperature, and in 1:15 at 100°, which solutions have no reaction on litmus paper, neither on phenolphthalein, methyl orange, tincture of coccionella, or logwood.—These solutions taste very faintly bitter to writer [J. B. N.] when five (5) c. c. has been swallowed.

Sulfonal is easily soluble in chloroform and in carbon disulfid; soluble in ether 1:135 at 15°; soluble in alcohol of 94 per cent., 1:65 at 15°, and 1:110 in alcohol of 50 per cent. at 15°. It crystallizes very well from a watery solution or from carbon disulfid.

(a) Chlorin water (Reagent 3) does not change it visibly; neither have Reagents 2, 4, 5, 6, 7, 15, 21 and 22 any effect upon it. No reactions are obtained in its watery solution by Reagents

11, 12, 13, 14, 16, 17, 18, 19 and 24. A five (5) per cent. barium nitrate solution does not give a precipitate in it.

(b) An odor suggestive of garlic (mercaptan) and likewise acid vapors, are liberated, when 0.050 g. Sulfonal is heated, very nearly to charring, in a glass tube, with one (1) g. of water-free sodium acetate, proving the presence of sulfur. A further reaction on sulfur in Sulfonal is, to cover the test tube in which the latter has been melted with dry sodium-acetate, with a piece of filter paper, previously moistened with a part of a solution of 0.10 g. nitro-prussid sodium ( $\text{Na}^2 \text{Fe} . \text{NO} . 5 \text{CN}$ ) in ten [10] c. c. of ten (10) per cent. ammonia; this paper becomes red, violet, and blue, the colors soon fading.

Or, substitute a piece of filter paper moistened with a ten (10) per cent. lead acetate solution, for the nitro-prussid sodium paper, which will become black.

Or, melt 0.10 g. Sulfonal with 0.20 of potassium cyanid in a test tube, notice the odor suggestive of garlic (mercaptan odor); cool; dissolve the slack in a few c. c. of water; acidulate with HCl and add a drop of Reagent 4; this gives a blood-red color reaction (sulfocyanate of iron).

(c) Manganous sulfate is formed when 0.20 g. Sulfonal is triturated with two (2) g. of a good commercial peroxid of manganese, slowly warmed at first and slightly heated afterwards, taking care to melt the subliming Sulfonal again and allowing it to flow back upon the  $\text{MnO}^2$ . Wash the residue with ten (10) c. c. of water, filter, and add to one part of the filtrate ammonium sulfid, whereby a flesh-colored precipitate is thrown down; add to another part a barium chlorid solution as Reagent on sulfuric acid.

### **Terpin Hydrate.**



Large crystals of the monoclinic system, melting at  $117^\circ$ , whereby they liberate water and form Terpin,  $\text{C}^{10} \text{H}^{18} (\text{OH})^2$ , melting at  $102^\circ$  and boiling nearly at  $258^\circ$ . Terpin hydrate, heated in a glass tube on a water bath, gives off vapors, condensing to

needles of Terpin. Terpin hydrate possesses a very slight aromatic odor, suggestive of pine leaves, and has a faintly bitter taste.

Is easily soluble in warm glacial acetic acid; in alcohol of 0.825 sp. gr., 1:13 at 20°; sparingly soluble in ether, chloroform and carbon disulfid; in water, 1:32 at 100°; in 1:250 at 15°. Its watery solution does not act upon litmus; a lead acetate solution gives a turbidity.

(a) It gives a red-yellow color reaction when strewn upon sulfuric acid (Reagent 21), thereby developing an agreeable aromatic odor—this odor is more prominent, when 0.10 g. Terpin hydrate is warmed nearly to the boiling point, with five (5) c. c. of diluted sulfuric acid (1.11 sp. gr.).

(b) Nitric acid (Reagent 15) does not act upon it in the cold, but a violent action takes place by warming Terpin hydrate with it.

(c) A rose-red color reaction is given when Terpin hydrate is evaporated in an open dish on the water bath, with a ten (10) per cent. sulfuric acid.

(d) Terpin hydrate gives a yellow color reaction, changing to brown and black-brown, when strewn upon a freshly made mixture of 0.020 g. ammonium molybdate and five (5) drops sulfuric acid (Reagent 21), spread out in a thin layer. A red to brown color reaction takes place if bismuth subnitrate is substituted for the ammonium molybdate. Titanic acid gives yellow to gold-colored tinges, if taken instead, and ammonium tungstate gives yellow, brown, gray or lilac colors.—Compare *Morphin*, page 76.

(e) A yellow color is obtained when a mixture of 0.005 g. Terpin hydrate and 0.10 g. sugar are triturated with three (3) drops of sulfuric acid (Reagent 21); this color fades by and by to a rose hue.

**Thallin Sulfate.\***

SULFATE OF OXIQUINOLINTETRAHYDROMETHYLETHER, OR SULFATE OF TETRAHYDROPARAQUIN METHYLPHENATE.

A not strictly white, but somewhat yellowish or brownish or ystalline powder with an odor suggestive of cumarin. Melting point  $110^{\circ}$ ; it solidifies crystalline, if allowed to cool; heated higher it chars, giving off vapors of an aromatic odor, which have an acid reaction to very sensitive litmus paper, and give a black spot on filter paper previously moistened with a ten (10) per cent. lead acetate solution. It browns when exposed to light. Is soluble, at the normal temperature, in 1:7 parts of water, which solution is acid to litmus, has a bitter salty taste, and leaves a dark brown residue (not the sulfate) when evaporated on the water bath.

It can, however, be recrystallized very well from a solution in warm chloroform; dissolves in alcohol of 0.83 sp. gr. 1:100, at the normal temperature; in much less proportions in warm alcohol, from which solution it recrystallizes, by cooling, in small crystals.

(a) Thallin sulfate colors chlorin water (Reagent 3) green, if strewn upon it; green flocks soon sink to the bottom; the mixture turns violet—see “(h)”. The same green coloring takes place with bromin water (Reagent 2); the precipitate is brown colored, however, redissolving with a green color on addition of more of the salt. In iodine water (Reagent 6), the salt is converted into a brown precipitate—see “(i)”.

(b) Reagent 12 gives a white, amorphous precipitate, in a watery solution, containing one-tenth of one (0.10) per cent. of the salt, that crystallizes in a few hours.

(c) Reagent 16 gives an amorphous precipitate in a one (1) per cent. watery solution of the salt, which soon crystallizes.

(d) Reagent 17 gives in a one (1) per cent. watery solution a red-brown precipitate which remains amorphous; the fluid becomes red.

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\*A name invented to take place of the cumbersome systematic name, and derived from the peculiar property of the salt to give many green color reactions. This name is unfortunately apt to be confused with Thallium sulfate, from Thallium (Tl).

(e) Reagent 24 gives a voluminous precipitate in one-half (0.5) c. c. of a one (1) per cent. watery solution, by adding slowly two and one-half (2.5) c. c. of the Reagent.

(f) Ammonia water (Reagent 1) gives a precipitate in a one (1) per cent. watery solution, soluble in excess of the Reagent.

(g) Lime water (Reagent 10) gives a precipitate in a five (5) per cent. watery solution, soluble in excess.

(h) Chlorin water (Reagent 3) gives a white turbidity in a one-tenth (0.1) of one per cent. solution of the salt; the fluid turns green at the same time.

(i) Iodin water (Reagent 6) gives in a one-tenth (0.1) of one per cent. solution of the salt a turbidity, whereby the fluid turns green, red afterwards.

(j) One (1) c. c. of Reagent 4 gives a green color, in the course of an hour, in one-half (0.5) c. c. of a one (1) per cent. solution of the salt, diluted with one-half ( $\frac{1}{2}$ ) liter (500 c. c.) of water. The color appears sooner and more brightly when more Thallin sulfate and less water is taken. The green fluid fades to a red and a yellow brown color. A one (1) per cent. watery solution of the salt, becomes by itself, without any addition, greenish-brown colored, when exposed to light and air.

(k) Thallin can be extracted from the watery solution of its salts by chloroform, when made alkaline.

(l) A brown filtrate is obtained, which colors the filter paper reddish, when 0.005 g. of the salt is agitated with 0.005 g. of a good commercial peroxid of manganese (90 per cent.  $\text{Mn O}_2$ ) and three (3) c. c. of water. The solution turns to a bright green, when a few drops of acetic acid (80 per cent.) are added, which color changes to brown and red; the red fluid is fluorescent.

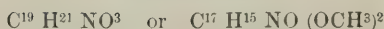
(m) A similar green fluid changing to red, is obtained if 0.005 g. of the salt are dissolved in two (2) c. c. of water with 0.050 g. of potassium iodate ( $\text{KIO}_3$ ) or of potassium ferri-cyanid.

The action is light, if potassium bromate ( $\text{KBrO}_3$ ) is substituted for the iodate; it sets in very soon however, if a few drops of acetic acid, 80 per cent., are added to the mixture.

(n) The salt dissolves colorless in sulfuric acid (Reagent 21), but a permanent red color reaction sets in, if a trace of nitric (Reagent 15) is mixed with the sulfuric acid.

(o) Thallin salts cause dark coloration of urine when given by the stomach or subcutaneously.



**Thebain.**

A crystalline powder, melting at  $193^\circ$  to a brown-red fluid, re-crystallizing when allowed to cool. It has a faint alkaline reaction when laid upon red litmus paper moistened with water; this reaction is sharper and appears sooner, if the alkaloid is moistened with alcohol.

Is easily soluble in alcohol (94 per cent.), chloroform and carbon disulfid at the normal temperature; less soluble in ether; yields well-formed crystals from a carbon disulfid solution.

Small crystals form in the filtrate, by cooling, when 0.20 g. Thebain has been boiled for a while with five hundred (500) c. c. of water [one-half liter], renewing the water that evaporates. This watery solution does not affect litmus paper, but has a bitter taste.

(a) Thebain is sensitive in this dilution to Reagents 2, 6, 7, 12, 16 and 24; but not to Reagent 17; it is nearly insoluble in cold water.

(b) It colors chlorin water (Reagent 3) red, when it is moistened with a small quantity of the Reagent; this red color fades to yellow when more of the Reagent is used.

(c) On nitric acid (Reagent 15) it gives a yellow color reaction.

(d) On sulfuric acid (Reagent 21) a permanent bright red color reaction.

(e) On hydrochloric acid (Reagent 5) it gives a greenish-yellow color reaction.

(f) The blue color which morphin gives with ammonium molybdate and sulfuric acid—see *Morphin*, page 75—is brown, when Thebain is treated, as described for morphin, and when bismuth subnitrate, titanin acid or tungstic acid is used; changing to green with the molybdate. A lilac color is obtained here as there.

(g) Thebain does not give a blue precipitate with the mixture of potassium ferricyanid and ferric chlorid as *Morphin* does—see page 76, “(g)”; in course of a few hours the reaction takes place, however, and sooner in direct sunlight.

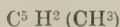
(h) Thebain does not liberate iodine from potassium iodate ( $\text{KIO}_3$ ) like *Morphin* does under the conditions described page 77.

(i) Small crystals of Thebanin hydrochlorid form in the yellow fluid in course of a few hours, if 0.20 g. Thebain [or Thebain hy-

drochlorid) is heated to boiling, with 1.4 c. c. of hydrochloric acid, of 1.124 sp. gr., and 2.8 c. c. of water, and the solution diluted, after the boiling, with four (4) c. c. of water. Thebanin hydrochlorid has the same formula as Thebain hydrochlorid, but is less soluble in water and colors sulfuric acid (Reagent 21) blue violet; ammonia water (Reagent 1) gives a brown precipitate in the mother liquor of these crystals, turning dark brown-red, when filtered off.

A one (1) per cent, watery solution of Thebain hydrochlorid is bitter and gives a choking sensation; has no reaction upon litmus paper. The salt is sensitive in this dilution, to all the reagents quoted above as producing precipitates or a turbidity in a watery Thebain solution; and also to the Reagents 13, 14 and 17. A saturated solution of sodium nitrate ( $\text{Na NO}_3$ ), used in large excess, gives also a turbidity, which clears up in the course of a few hours, while Thebain forms crystals. A saturated watery solution of an equally easily soluble salt, as *e. g.* potassium iodid (KI) does not have the same result or has it less satisfactorily. Thebain salicylate forms as a granular precipitate of microscopical crystals, when a sodium salicylate solution is used.

### Theobromin.



#### DIMETHYLBXANTHIN.

A light, white, somewhat crystalline powder of a bitter taste. It chars at 300° without previous fusion, whereby it gives off vapors of an alkaline reaction to red litmus paper, and also amorphous sublimation products.

Theobromin does not act upon litmus. It is soluble in 1:70 parts of water at 100°, but only microscopically small crystals form in this solution, when allowed to cool slowly; the tasteless filtrate contains in 1600 parts, one (1) part Theobromin.

Reagents 2, 6, 7, 11, 12, 13, 14, 16, 17 and 22 have no effect upon it, in this dilution.

It is sensitive to Reagent 24; a few drops of it, added to two

[2] c. c. of the watery Theobromin solution, give a precipitate, soluble in an excess (one c. c.).

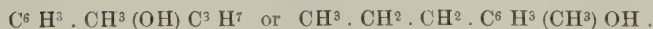
Is very little soluble in alcohol of 0.793 sp. gr., at 20°; much less in ether and in benzene; slightly in chloroform and in carbon disulfid; insoluble in petroleum ether; fairly soluble in glacial acetic acid.—Chloroform is comparatively the best solvent. Neither nitric or sulfuric acid act upon it.

(a) Theobromin yields a similar product to caffein, if treated with potassium bromate (KBr O<sub>3</sub>) and acetic acid, as described under *Caffein*, page 26 “(g)”.

(b) 0.020 g. Theobromin dissolves in two (2) c. c. of ammonia water (Reagent 1) by slightly warming; small, white, crystalline needles form in this solution in the course of a few hours, if two (2) drops of a saturated watery solution of silver nitrate are added, and the mixture kept in a loosely corked test tube in a water bath. This compound (C<sup>7</sup> H<sup>7</sup> Ag N<sup>4</sup> O<sup>2</sup>)<sup>2</sup> + 3 H<sup>2</sup>O, does not dissolve when it is heated with the mother liquor to the boiling point, after a dilution with ten (10) c. c. of water. It can be dried without decomposition, at 100°.

(c) If 0.010 g. Theobromin is dissolved in two (2) c. c. of diluted and slightly warmed nitric acid of 1.06 sp. gr., two (2) drops of the saturated, watery silver nitrate solution added to the solution, cause only a slight turbidity. Large, crystalline needles form in course of an hour, of the formula, NO<sup>3</sup> H (C<sup>7</sup> H<sup>8</sup> N<sup>4</sup> O<sup>2</sup>) NO<sup>3</sup> Ag, that are soluble in concentrated nitric acid, and in boiling (not in cold) water.

### Thymol.



#### PROPYLMETAKRESOL.

Large sized crystals with an odor of thyme and of a sp. gr. of 1.06; they melt at 50° (50°), remaining liquid for quite a while; rubbed, they develop electricity, attracting small pieces of paper. Thymol sinks in water,—camfer floats; Thymol boils at 230° and sublimes in a glass tube, unaltered. Very easily soluble in ether

alcohol, chloroform, acetic acid, carbon disulfid and warm glycerol; soluble in water, 1:1000, which weak solution has a strong odor of Thymol and its peculiar burning, aromatic taste; is superior to phenol and eucalyptol in antiseptic properties, in this dilution.\* It liquefies when triturated with chloral hydrate.

(a) Bromin and chlorin water (Reagents 2 and 3) give strong precipitates in the watery solution. Iodin water (Reagent 6) and a ten (10) per cent. lead acetate solution, cause only a slight turbidity.

(b) Nitroso-thymol (Thymoquinonoxim)— $C^3 H^7 C^6 H^2 O(NOH) CH^{13}$  is formed, when 0.005 g. of Thymol is triturated with 0.010 g. of potassium nitrite or sodium nitrite and to this mixture is added two (2) c. c. of sulfuric acid (Reagent 21). The compound remains in solution, which becomes brownish-yellow colored at first and soon takes a permanent, dark green color. It is slightly soluble in water. A few drops of this green acid solution dropped into ten (10) c. c. of water at  $20^\circ$ , change from green to a blood-red; a few drops more cause a turbidity; a red-brown, flocculent precipitate is obtained when the two (2) c. c. of the acid are added at once to the ten (10) c. c. of water.

(c) An intense pink colored fluid of a permanent color is obtained when one (1) c. c. of chloroform, U. S. P.—containing one (1) per cent. of alcohol—is poured upon a mixture of 0.01 g. Thymol and 0.010 g. caustic potash or soda.

(d) A black residue is obtained if a solution of 0.010 g. Thymol in five (5) drops of alcohol of 94 per cent., to which one drop of Reagent 4 has been added, is evaporated on a water bath to dryness. This black residue dissolves in one (1) c. c. of alcohol of 94 per cent. with a brown color, leaving only a very few particles undissolved.

(e) A turbid, violet colored mixture is obtained when a mixture of 0.005 g. Thymol and 0.010 g. potassium nitrite or sodium nitrite is warmed in a test tube for about ten minutes to  $75^\circ$  or  $80^\circ$  with one (1) c. c. of Reagent 13, diluted with two (2) c. c. of water.

(f) Thymol can be recrystallized from water when one half (0.5) g. Thymol is boiled with two hundred and fifty (250) c. c. of

\*Nothnagel & Rossbach, pages 454-459; Handb. d. Arzneimittellehre, 6th Auflage, Berlin, Hirschwald, 1887; Ewald, Arzneiverordnungslehre, page 697, 12th Auflage, Berlin, A. Hirschwald, 1892.

water, filtered, and the fluid allowed to cool. The mother liquor has a green color by reflected light, when ten (10) drops of Reagent 4 are added to twenty-five (25 c. c.) of the fluid; the color is not constant and soon makes place for a white turbidity, in consequence of the forming of dithymol,  $C^{20}H^{26}O^2$ .

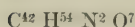
(g) An intense, permanent bluish-green color reaction takes place when a small particle of Thymol is dropped into a mixture of one (1) c. c. of glacial acetic acid, four (4) drops of sulfuric acid (Reagent 21), and one (1) drop of nitric acid (Reagent 15)—menthol and camfer give no color reaction when similarly treated.

(h) 0.50 g. Thymol, triturated with twelve (12) drops sulfuric acid (Reagent 21), gives a yellowish-red fluid, solidifying in about four hours to a hard carmine red, crystalline mass of  $\alpha$ -Thymol—sulfonic acid— $C^6H^2(OH)CH^3$ .  $C^3H^7$ .  $SO^2(OH)$ . A small particle of this red compound, dissolved in fifty (50) c. c. of water, to which previously one (1) drop of Reagent 4 has been added, colors the water violet.

Add now six (6) c. c. water to the red compound, whereby it loses nearly all its color; warm the mixture to about  $70^\circ$  to  $80^\circ$ ; add 1.50 g. white lead ( $PbCO^3$ ); agitate; filter; divide filtrate into three (3) parts. To part *one* add five (5) drops of ten (10) per cent.  $H^2SO^4$ , which gives a white precipitate of sulfate of lead; to part *two*, add one (1) drop of Reagent 4, which gives a violet color reaction; to part *three*, add five (5) drops nitric acid (Reagent 15), whereby it becomes dirty, dark green colored, which color changes to a chrome yellow, by warming to about  $75^\circ$ .

(i) A kermes red precipitate of dithymol diiodid is formed, when a solution of 0.50 g. of iodine and 0.65 g. of KI in ten (10) c. c. of water, is added to a solution of 0.150 g. Thymol in two and a half (2.5) c. c. of a ten (10) per cent. caustic soda solution. The same reaction occurs when five (5) g. Thymol, five (5) g. KI and five (5) g. of Na OH are dissolved in fifty (50) c. c. of water by warming, and this solution poured into two hundred and fifty (250) c. c. of a strong solution of hypochlorid of soda (so-called Labarraque solution).



**Tritopin.**

Forms perfect short prisms, melting at  $102^\circ$ , that give a blue spot on moist, sensitive, red litmus paper. Easy soluble in chloroform; less so in alcohol of 94 per cent. and in 10 per cent. caustic soda solution; sparingly in ether; insoluble in carbon disulfid.

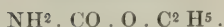
(a) Tritopin gives a rose-red color reaction when strewn upon sulfuric acid (Reagent 21), which color increases in time. The color changes to green, blue and violet, by warming on the water bath or over a flame.

(b) A bright violet red color reaction is obtained, if a trace of ferric chlorid (Reagent 4) is added to its solution in sulfuric acid (Reagent 21), with a glass rod of the size of a match. The color is dark red when a trace of sodium nitrate ( $\text{Na NO}^3$ ) is substituted for the ferric chlorid ( $\text{Fe}^3 \text{Cl}^6$ ).

(c) It gives a brown color reaction, when treated with sulfuric acid and bismuth subnitrate, as described for *Morphin* and *Laudanosin* (page 76 and page 71 respectively), which brown color changes to red and then to yellow-brown. With ammonium molybdate and sulfuric acid, and with titanio acid, it gives a lilac color.

(d) It reduces ferric chlorid to a ferrous compound in the mixture of ferric chlorid and potassium ferricyanid, and gives a blue precipitate under the conditions described under *Morphin*, page 76.

(e) It liberates also iodine from potassium iodate ( $\text{KIO}^3$ ).—Compare *Morphin*, page 77.

**Urethan.\***

## ETHYL CARBAMATE.

Crystallizes in large tables, melting at  $50^\circ$ , boiling at about  $180^\circ$ ; to writer it has a faint odor, suggestive of a fruit ether [J. B. N.]; to others it is odorless; it has a cool, salty taste, suggestive of saltpeter; has no action upon litmus.

Is soluble in equal parts of water, of ether and in a little more of chloroform; in less of alcohol of 94 per cent.; in carbon disulfid, it is soluble by warming only, and Urethan forms in large crystals, when the solution is allowed to cool. It lowers the temperature a few degrees when dissolved in water; three (3) g. of salt, dissolved in twenty-five (25) c. c. of water of  $20^\circ$ , lower the temperature two (2) degrees.

Not any of the common reagents have effect upon it in substance or in a watery solution; lime water, caustic soda solution and sulfuric acid excepted.

(a) It liberates  $\text{NH}^3$ , when 0.100 g. Urethan is dissolved in ten (10) drops of Reagent 20 or in ten (10) c. c. of Reagent 10; slowly in the cold, more quickly by warming.

(b) 0.10 g. Urethan is decomposed—liberating carbon dioxid—by ten (10) drops sulfuric acid (Reagent 21), not at the water bath temperature, however, but when heated; the mixture foams thereby.

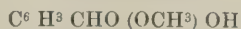
(c) One (1) c. c. of Reagents 13 or 14 can be mixed with one (1) c. c. of a ten (10) per cent. watery solution of the salt without producing any action; but a white flocculent precipitate of carbamate of mercury, not yellow or red mercuricoxidhydrate, sinks slowly to the bottom, when one (1) c. c. of Reagent 20 is added. It remains white by boiling. No precipitate is formed when Reagent 11 is substituted for Reagents 13 and 14.

(d) Iodoform is formed, when 0.10 g. of iodine, in small portions, is added to a solution of 0.20 g. of Urethan, dissolved in two (2) c. c. of a warm ten (10) per cent. caustic soda solution. If the

\*"On the Pharmacological Action and Therapeutic Application of some Ethereal Salts of Carbamic Acid," by Dr. O. Schmiedeberg, an abstract of which will be found in *Pharm. Journal and Transactions* (London, 1885), page 641, Vol. XVI.

well-known, fine yellow crystalline precipitate of iodoform does not form right away, a few particles more of iodine will have to be added to the solution, until it is slightly yellow colored. The iodoform is verified under the microscope by the hexagonal crystal form of the particles. This test has to be made strictly according to the description, or other compounds form. The salt has mild hypnotic properties.

### Vanillin.



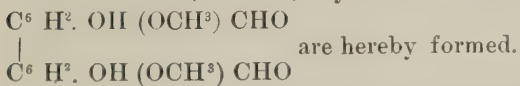
#### METHYLPROTOCATECHUALDEHYD.

Crystalline needles of a powerful aromatic odor and taste, melting at  $81^{\circ}$ ; they can be sublimed without charring; the vapors have an acid reaction on moist blue litmus paper.

Vanillin is easily soluble in ether, alcohol, chloroform and carbon disulfide; in water, 1:100, at  $15^{\circ}$ , 1:20 when warmed on a water bath.

(a) A small particle of Vanillin, added to a solution of 0.010 g. of pyrogallol in one (1) c. c. of hydrochloric acid (Reagent 5) heated to boiling, gives a bright violet-red color reaction; phloroglucin, resorcinol or thymol can be substituted for pyrogallol in this test.

(b) A blue fluid is obtained when 0.020 g. of Vanillin is agitated with two (2) c. c. of water, to which one (1) drop of Reagent 4 has been added. The blue color turns brown when the fluid is warmed. Small, flexible, crystalline needles of dehydrodivanillin



A warm solution of 0.010 g. of Vanillin in ten (10) c. c. of water, to which one (1) drop of Reagent 4 is added, becomes brown-red, *not blue*.

(c) Dissolve 0.010 g. of Vanillin in one hundred (100) c. c. of water "(A)"; add to ten (10) c. c. of this solution, representing  $\frac{1}{10000}$  (0.0001), one (1) c. c. of a one (1) per cent. ferrous sulfate solution, and then one (1) drop of bromine water (Reagent 2). The fluid becomes deep bluish-green colored.

With one-tenth (0.1) c. c. of the one (1) per cent. ferrous sulfate solution added to one (1) c. c. of the 1:0.0001 g. of Vanillin solution, the coloring is not so good or so easily noticed as in a large quantity.

The reaction is not as good when bromin water is added first and the ferrous sulfate solution afterward.

With chlorin water it is a light green color reaction. The limit for sensitiveness of Vanillin to this reaction is 0.00001 (1:100,000) of a gram. A faintly bluish-green color reaction is to be seen in a part of the ten times diluted solution "A".

(d) A yellow solution, which becomes slowly red colored is obtained by warming 0.005 g. Vanillin with three (3) c. c. of Reagent 14 and 0.010 g. of sodium nitrite ( $\text{NaNO}_2$ ). The color is dark violet, if one (1) c. c. of Reagent 13, diluted with two (2) c. c. of water, is substituted for Reagent 14.

(e) Vanillin dissolves in sulfuric acid (Reagent 21) with a yellow color; it colors nitric acid (Reagent 15) yellow-red when strewn upon it; small, brown crystal conglomerates form in the fluid.

### Veratrin.

This mixture of alkaloids in commerce called Veratrin and veratrinum purum, has fairly constant properties; it is highly irritating to the nostrils. It is easily soluble (1:4) in alcohol of 94 per cent., at the normal temperature, and more so (1:2) in chloroform; less in ether (1:10), amyl alcohol, benzene and carbon disulfid; in water 1:1500. On moist red litmus paper, it gives a blue spot. A 1:10,000 watery solution is alkaline to tincture of coccionella (1:10), not to phenolphthalein solution (1:100).

(a) 0.005 g. of Veratrin added to five (5) c. c. sulfuric acid (Reagent 21) becomes lumpy and yellow colored; violet on warming the solution; this color increases to orange and cherry-red, and slowly the acid becomes thus colored. Sensitive on a 1:0,000,001 ( $\frac{1}{1000000}$ ) part of a gram.

To verify this color test, dissolve 0.10 g. Veratrin in one hundred (100) c. c. of alcohol of 94 per cent.—solution "A."

Dilute one (1) c. c. of this solution with water, to one hundred (100) c. c., solution "B"—1:1,000,000 g. Evaporate one (1) c. c. solution "B" to dryness; add to the cooled residue one (1) drop of sulfuric acid (Reagent 21), when a faintly yellow color reaction takes place; the yellow, orange and cherry-red color reactions are very strong with 0.00001 g. of Veratrin in the cold; when warmed in an air bath to 100°, a constant purple color reaction will be seen. For days a green-yellow fluorescence is to be noticed at the same time, along the sides of the test tube, when the tube is agitated to dissolve the Veratrin and a film of acid attaches to the sides. This fluorescent property becomes more prominent when five (5) c. c. more of the acid is added to the cherry-red solution.

(b) 0.005 g. Veratrin gives no color reaction in the cold with five (5) c. c. of hydrochloric acid (Reagent 5); by warming it over the flame, the solution colors pink-red—constant for months; 0.10 g. Veratrin, boiled with five (5) c. c. of the acid, gives a purple-red color reaction. This red color appears also, after a certain time in the cold, and is permanent. The solution is not fluorescent, as the sulfuric acid solution is, but can be made temporarily so by adding two (2) drops of glacial acetic acid.

(c) A blood-red colored fluid is obtained, solidifying to a slightly yellow-colored salt, when 0.10 g. oxalic acid is carefully melted in a glass tube, and 0.005 g. Veratrin added to the melted acid and warmed further.

(d) 0.10 g. Veratrin warmed on the water bath, with one (1) c. c. of phosphoric acid, of 1.4 sp. gr., colors purple-red, and gives off an odor suggestive of butyric acid.

(e) A dark green color reaction, followed by reddish-purple and blue colors, is obtained by adding a sprinkling of finely-powdered sugar to a solution of Veratrin in sulfuric acid (Reagent 21). This reaction is sensitive to 0.00001 g. of Veratrin. Not a dark green color reaction takes place in this dilution, but a decided grass-green color, followed by purple and blue colors. It becomes, however, brown very quickly and blackens. It is seen at its best with a 0.0001 g. (1:10000).

I. Evaporate one (1) c. c. of solution "A" to dryness. Add to the residue two (2) drops of sulfuric acid (Reagent 21). Spread the acid in a thin film. Add the sugar (0.010 g).



II. Evaporate one (1) c. c. of a dilution of "A" with nine (9) c. c. of water; take one (1) c. c. of this dilution. Treat as under I. The blue color fades in the course of a few hours to a dirty violet or blackens—from the action of the sulfuric acid upon the sugar.

Blue-colored compounds are insoluble in ether, chloroform and carbon disulfid. Different substances prevent this test—Licorice for instance.

The above described reactions are useful in an examination as to the identity of a fluid extract or a tincture veratrum (white hellebore). They can be obtained very good from 0.20 g. sabadilla seeds. Percolate 0.20 g. of unground sabadilla seeds with a few c. c. of strong alcohol acidulated with acetic acid; dilute percolate with one (1) c. c. of water and evaporate to a minimum (1 c. c.) Veratrin is plainly to be detected in this residue. Fluid extract of white hellebore or tincture of veratrum are to be evaporated to dryness on the water bath, the residue taken up with water, acidulated with acetic acid, filtered, and the filtrate submitted to the test on Veratrin.

THE END.

#### ADDENDUM.

Footnote on page 116.

Pure, dry, Resorcinol was repeatedly found in our laboratory, to have a meltingpoint of  $114^{\circ}$ .

J. B. N.



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